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1961
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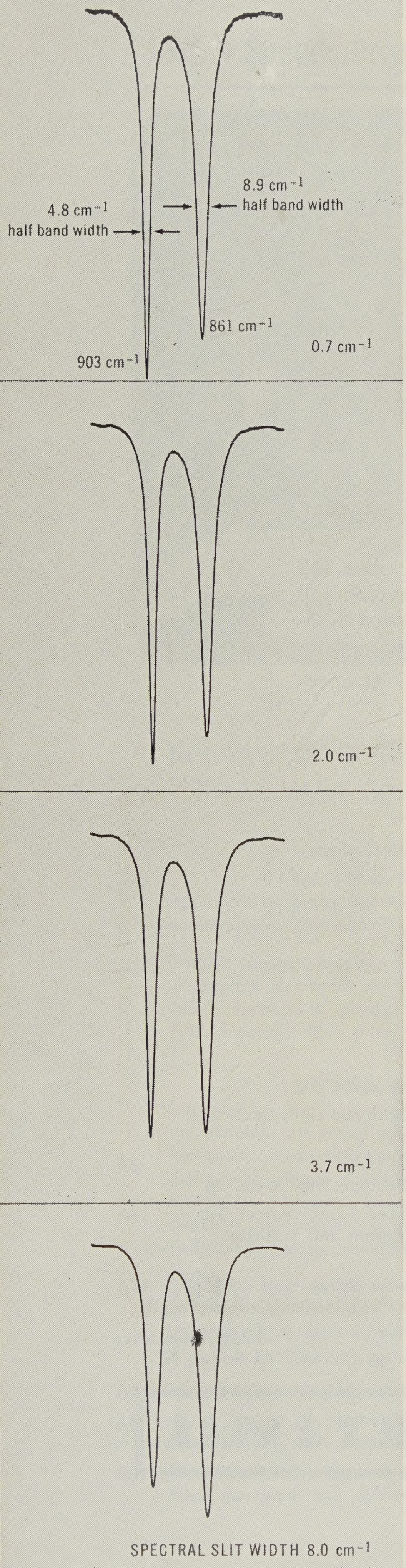

Left, spectrum of a 0.21 mm. thickness sample of spectro-grade cyclohexane demonstrates the importance of high resolution for routine *quantitative analysis.*

Right, the C-H stretching band of methane illustrates the increased research *data obtainable with high resolution spectroscopy.*

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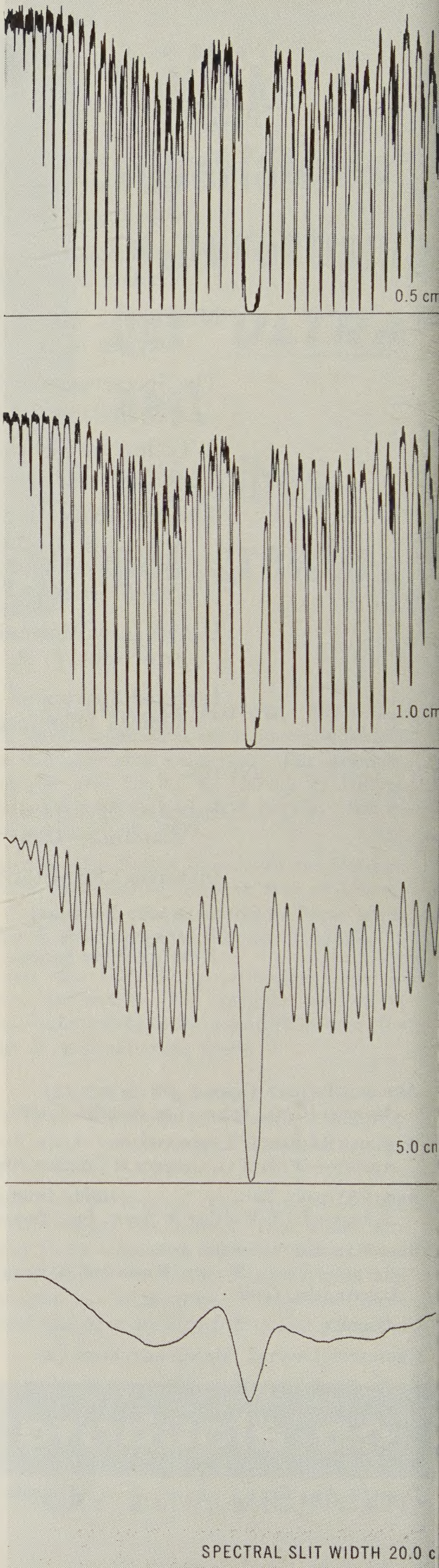


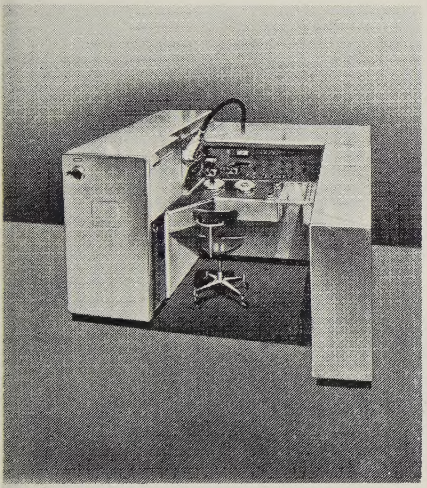
What's New?

Editor—Rodger W. Loofbourow

[Contributions for this column should be sent to its Editor, Mr. Rodger W. Loofbourow, Crobaugh Laboratories, 3800 Perkins Avenue, Cleveland 14, Ohio.]

A new, improved *Electron Probe Microanalyzer* has been announced by Philip's Electronic Instruments, Mount Vernon, N. Y.

In this instrument the cross section of the electron beam is adjustable in the range from 0.1 to 100 microns. Curved crystal X-ray spectrograph techniques are used and read-out is by scaler or chart recorder. The internal light optics system provides magnification to 300X while the specimen is in the analyzing position. Facilities are provided for the simultaneous determination of three elements and the limit of detectability is claimed to be about 0.1 to 0.01%.



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Introduction of the Type 24-510 *Radiflo Leak Detector* for high efficiency production-line testing has been announced by the Analytical and Control Division of Consolidated Electrodynamics Corporation, a subsidiary of Bell & Howell Company.

This instrument is designed to test hermetically sealed components for leaks in the 10^{-11} atm-cc/sec range. Large capacity, short activation period, and automatic operation make it possible to test as many as 10,000 transistors in a single activation of less than one hr. In the activation stage the components are sealed in a lead lined chamber and flooded with a radio active tracer gas, krypton 85, under pressure. After the "soak" period the gas is removed, the components are air washed and tested on an individual or multiple unit basis.

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(Continued on page 13A)

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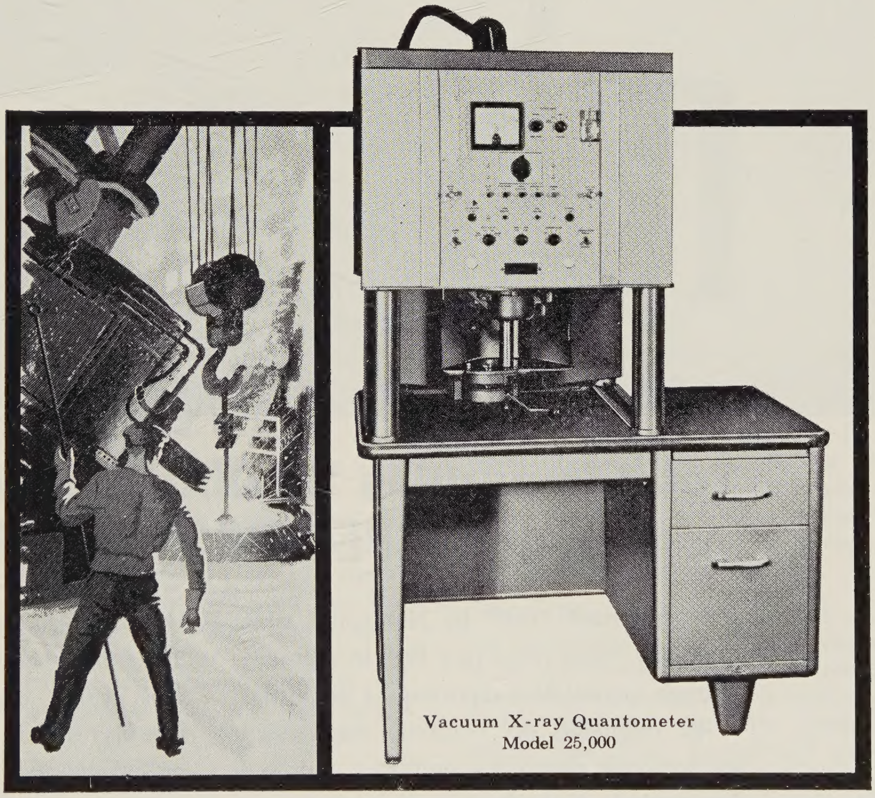

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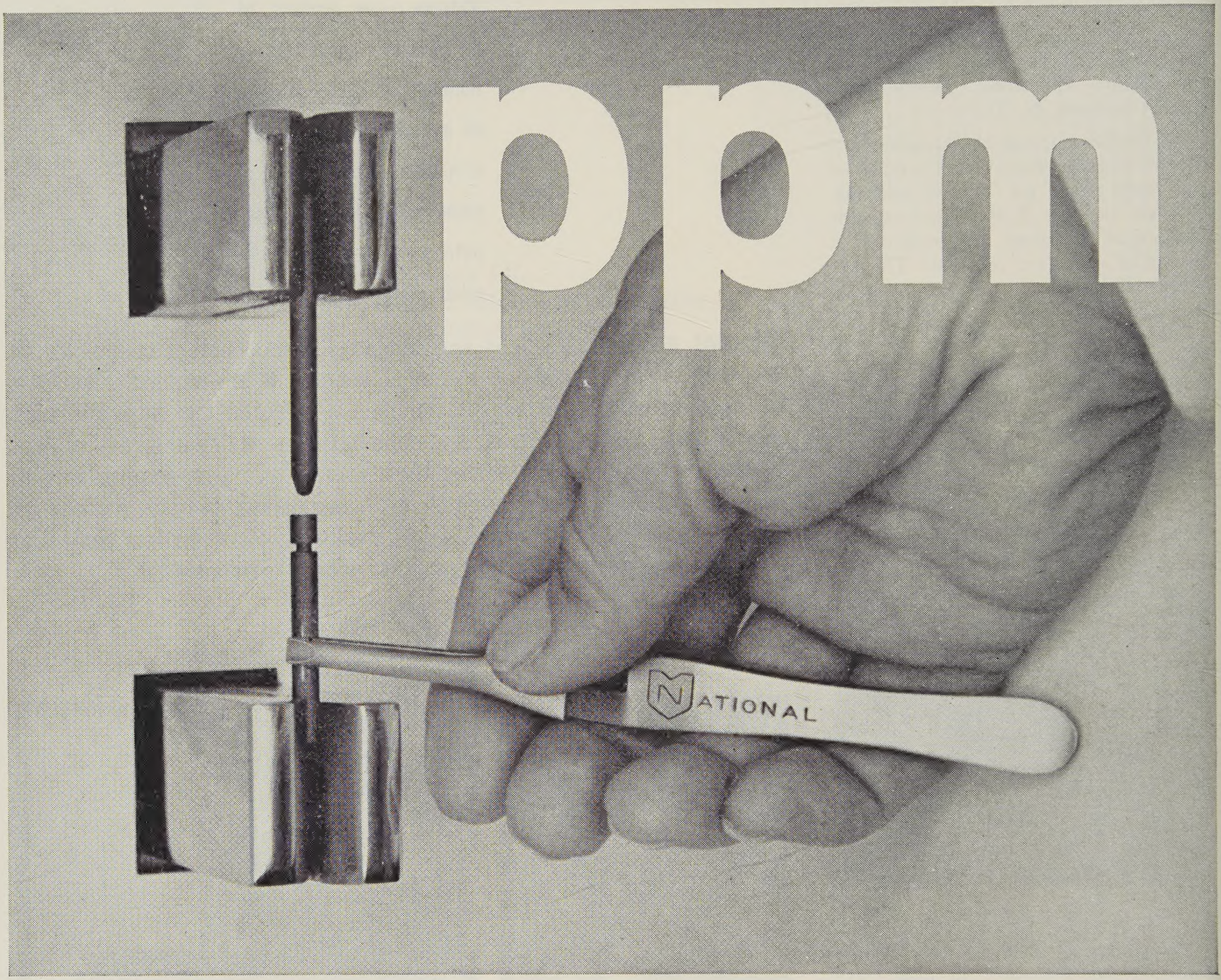

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The Spectral Line

Editor—S. Richard Wiley

[News about members and matters of interest to spectroscopists may be sent to the Editor, S. R. Wiley, 1239 Owen Brown Rd., Ellicott City, Md.]

Dr. George H. Morrison is well known by spectroscopists of the New York metropolitan area for the outstanding analytical work, which he managed at General Telephone and Electronics Laboratories, Bayside, N. Y. He has joined the staff at Cornell University as Professor of Chemistry, where he will be in charge of the analytical program of the new Material Science Center. This new research organization is expected to be one of the most important of its kind in the world.

Dr. Morrison has an exceptional background in trace analysis and in the use of many types of instrumentation. His use of the wide aperture high speed spectrograph to analyze parts per billion concentrations of impurities in semi-conductor materials has received much attention. Dr. Morrison has served with the Manhattan Project and the U.S. Atomic Energy Commission prior to his association with General Telephone and Electronics Laboratory.

Dr. Morrison's education includes a B.A. from Brooklyn College and Ph. D. from Princeton University. He has taught at Rutgers University and Adelphi College. He served as General Chairman of the 1960 Eastern Analytical Symposium, and is Chairman-Elect of the Metropolitan Long Island Subsection of the A.C.S. and is a councilor of the Division of Analytical Chemistry of A.C.S.

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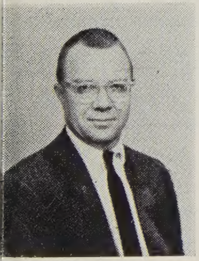
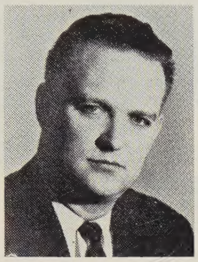


John Udaloy of Arlington, Mass. has been elected to the position of Vice President-operations, Jarrell-Ash Company, Newtonville, manufacturers of spectrochemical equipment. In his new assignment, Mr. Udaloy will assume direction of the Sales, Production, Engineering and Research departments of the company.

Mr. Udaloy is a graduate of Harvard College, B.S. 1950, and the Harvard Business School, M.B.A. 1952. He joined Jarrell-Ash Company in March, 1960 as Assistant To The President.

——— λ ———

The two new Vice Presidents, who have been elected at Perkin-Elmer Corporation, are *Henry F. Brockschmidt*, General Manager of International Operations and *Robert H. Sorensen*, General Manager of the Electro-Optical Division.



Mr. Brockschmidt has been General Manager of International Operations since 1958. He joined the company in 1951 as assistant director of production, was assigned to the firm's foreign operations in 1955, and became director of manufacturing for the Instrument Division in 1956. Earlier he had been with Barber-Colman Co. and on the staff of the M.I.T. Radiation Laboratory. Perkin-Elmer has manufacturing subsidiaries in West Germany and England, sales subsidiaries in four other European countries, and has just formed a joint company in Japan with Hitachi, Ltd.

Mr. Sorensen joined Perkin-Elmer in 1959 as assistant to the Executive Vice President. He was named General Manager of the Electro-Optical Division earlier this year. Before joining Perkin-Elmer he was with the Remington Rand Univac Division of Sperry Rand Corporation where he served as assistant to the vice president for engineering. He also had been manager of the Univac Division's Norwalk, Conn. operations. Perkin-Elmer's Electro-Optical Division develops and produces precision optics and electronic-optical systems, primarily for space and defense programs.

Chester W. Nimitz, Jr. has joined the company as a Vice President and General Manager of the firm's Instrument Division. Mr. Nimitz resigned from Texas Instruments, Inc. to accept the position.

——— λ ———

Eugene K. Thorburn has been appointed to the Senior Technical Staff of the West Coast Operation of the Electro-Optical Division, Perkin-Elmer Corporation. Mr. Thorburn was formerly Vice President and Chief Engineer of Pacific Optical Corporation, where he was responsible for the design and manufacture of high acuity optical systems.

Mr. Thornburn's career in the optical field began at Tinsley Laboratories in 1939, where he supervised the production of optical components for military end-items until 1944. Following his military service in the United States Navy, he was associated with Bausch and Lomb Company for four years designing microscope systems. Later he served two years at the Northrup Aircraft Optical Laboratory in Pasadena and contributed in the design, fabrication, and test of the Snark Guidance System. Prior to joining Pacific Optical in 1953, he was appointed Optical Division Leader for Pacific Mercury Research Center in Santa Barbara.

Mr. Thorburn attended Lassen Junior College, University of California, and received his B.S. degree in Optics with distinction from the University of Rochester in 1950.

——— λ ———

Robert T. O'Connor has been named Acting Chief of the Cotton Physical Properties Laboratory, Southern Utilization Research and Development Division of the U. S. Department of Agriculture. The Cotton Physical Properties Laboratory is concerned with cotton fiber physics, microscopy, textile testing, and spectroscopy.

Mr. O'Connor has devoted his entire 20 years at the Southern Division to the application of highly specialized methods and instruments for studying both natural and chemically modified cotton and other agricultural products. He has been particularly active in the field of spectroscopy where he is widely known as a specialist and for which work he was honored with the Department's Distinguished Service Award. The author of 111 scientific papers, Mr. O'Connor is a consultant to the Graduate School of Tulane University.

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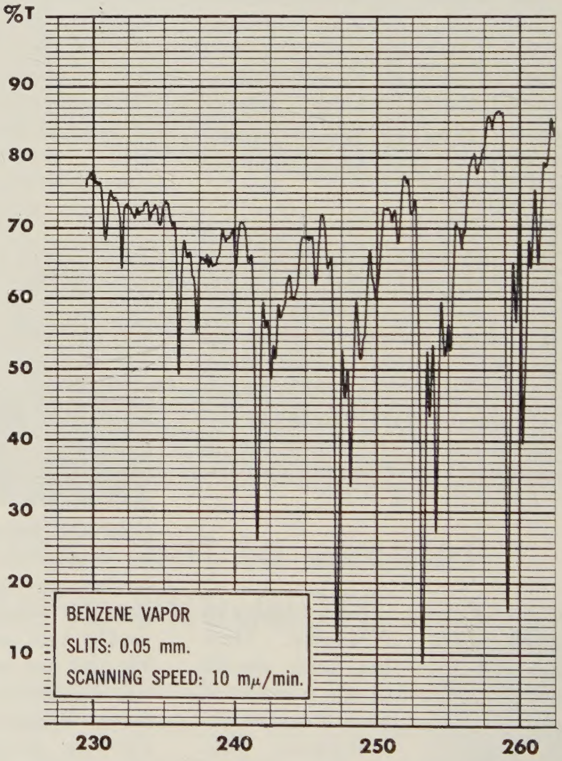

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Far Ultraviolet Spectroscopy. I. Modification of the Beckman DK Spectrophotometer for Automatic Transmittance Recording in the Region 1700-2000 A

Wilbur I. Kaye

Beckman Instruments, Inc., Fullerton, California

Abstract

Abundant opportunities exist for analytical and molecular structure studies using the far ultraviolet region of the spectrum since almost all compounds in the vapor state possess intense, characteristic, and often detailed absorption spectra. Unfortunately, the experimental difficulties in working in this region have discouraged its widespread use. Beckman Model DK-1 and DK-2 spectrophotometers have been modified to perform to 1700 A for the automatic recording of relative transmittance spectra. This performance has been accomplished through the use of very high quality quartz and fused silica for prisms and windows. The absorption of the atmosphere in the optical path has been eliminated by purging with nitrogen. The resolution achieved is remarkably good, because of the high dispersion of quartz in this region. Except for the necessity of purging, the experimental difficulties of working to 1700 A are little different from those in near ultraviolet spectroscopy.

Introduction

The far ultraviolet region of the spectrum extends from approximately 2000 A, the edge of the near ultraviolet, to approximately 100 A, the upper limit of the x-ray region. Experimental difficulties in obtaining quantitative spectra in this region increase with decreasing wavelength. There are no really satisfactory sources of continuous radiation for use below 1650 A although some progress is being made here. No practical window materials are available for use below 1050 A. However, down to about 1700 A quantitative spectra may now be obtained with little more effort than is required for near ultraviolet study. In view of the very intense, sharp, and characteristic absorption spectra that almost all gases possess in this region, it is bound to be more widely used in the future. Some applications are discussed in the second paper of this series (*1*).

Briefly, the Beckman DK-1 and DK-2 spectrophotometers have been modified to perform in the far ultraviolet by using very high quality quartz prisms, special windows on the sources, detectors and sample cells, and purging of the entire optical path of the instrument with nitrogen (*2*). It has been found desirable to change the slit curvature. Auxiliary drive systems for slower scanning rates have been found advantageous. The extreme dispersion of quartz in the far ultraviolet results in excellent resolution.

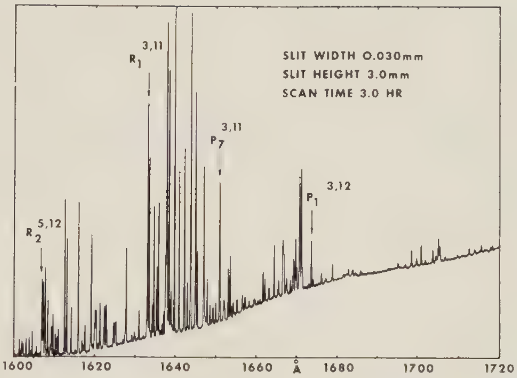

Fig. 1. Energy Spectrum of Hydrogen Lamp

The most serious difficulties in developing this instrument have centered about the reduction of stray light, since the far ultraviolet radiation passing the exit slit is a very small part of the total radiation emitted by the source and sensed by the detector. Fortunately these problems have been solved without impairing in any way the performance of the instrument in the near ultraviolet, visible, and near infrared regions.

Since the development of this instrument has required the study of almost every component of the instrument, each of these will be discussed separately.

Instrumentation

Source

The hydrogen discharge lamp emits a continuum from about 3600 to 1650 A. Above and below this region it emits a very complex line spectrum. Unfortunately, the envelope of the standard Beckman hydrogen lamp is opaque below 1850 A. By the use of selected Suprasil fused silica for the window the lamp may be used to 1590 A. The Suprasil requires the use of graded seals and this has dictated a longer length to the lamp. The source housing has been completely redesigned, because of this increased length and the necessity of purging the optical path.

Figure 1 shows the spectrum of radiation from this lamp (Beckman No. 94055) in the far ultraviolet. Discrete emission lines are superimposed on the continuum beginning at 1710 A, but they are relatively weak down to 1650 A. The emission lines below 1650 A are so much more intense than the continuum that this source is poor for absorption studies below this wavelength in the presence of stray light. The relative intensity of discrete versus continuous radiation is a function of the resolution used. The relative stray light varies inversely proportional to the source intensity; consequently the emission lines from the source look like absorption bands when absorption spectra are run below 1650 A. The more exotic sources such as the Lyman discharge and the Tanaka rare gas continua lamps have not been used. The literature of these sources has recently been reviewed by W. C. Price (*3*).

The far ultraviolet emission spectrum of hydrogen has been most recently studied by Herzberg and Howe (*4*). The emission lines are due to vibrational and rotational fine structure superimposed on the electronic transitions of the hydrogen molecule. These authors tabulate the bands to a hundredth of a wavenumber. Unfortunately, their data are largely tabular, and identification of some of the lines is difficult. The older spectra published by Hyman (5) and the fine photographs of the far ultraviolet hydrogen spectrum taken by Schumann and published by Lyman (6) are useful. They show emission lines from 1675 and 1268 A. The lines on Figure 1 utilize Hertzberg and Howe's data.

The Beckman far ultraviolet source has been filled with deuterium and its spectrum determined. Of course, the discrete molecular emission lines occur at slightly different wavelengths. Aside from the fact that the intense emission lines begin about 20 A shorter wavelength than those of hydrogen, there is little advantage in the use of deuterium.

Prism

The prism used in the DK instruments measures 1 in. on the base, 1 in. on the height, and 2 in. on the hypotenuse. The apex angle is 30°. It is made of crystalline quartz, and the back aluminized surface is normal to the optic axis. Figure 2 shows the relative transmittance spectrum of two samples of quartz and a curve of theoretical reflection loss only. Curve B is a typical transmittance curve of the best synthetic quartz. A very small fraction of the available natural quartz approaches this transparency. Curve C is a curve of natural quartz acceptable for use in the Model DU spectrophotometer. While there is a vast difference between curves B and C, the C curve represents nevertheless a high grade of Brazilian quartz. The synthetic quartz is grown from solution at high temperature and pressure. An account of the hydrothermal process for growing this quartz has been given by Buehler (*7*). Any quartz with a 30% or better transmittance in one in. thickness at 1700 A is acceptable for use in far uv DK instruments as far as transparency is concerned.

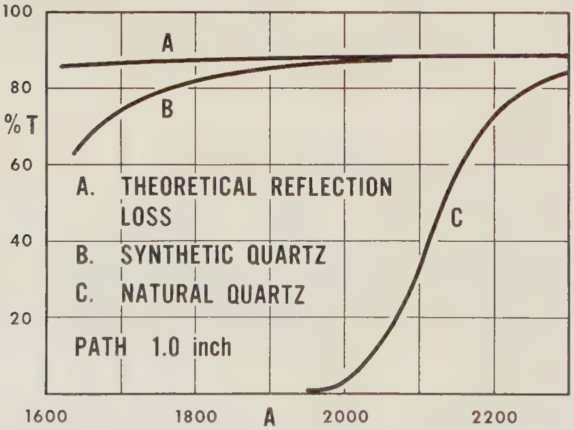

Fig. 2. Transmittance of Quartz

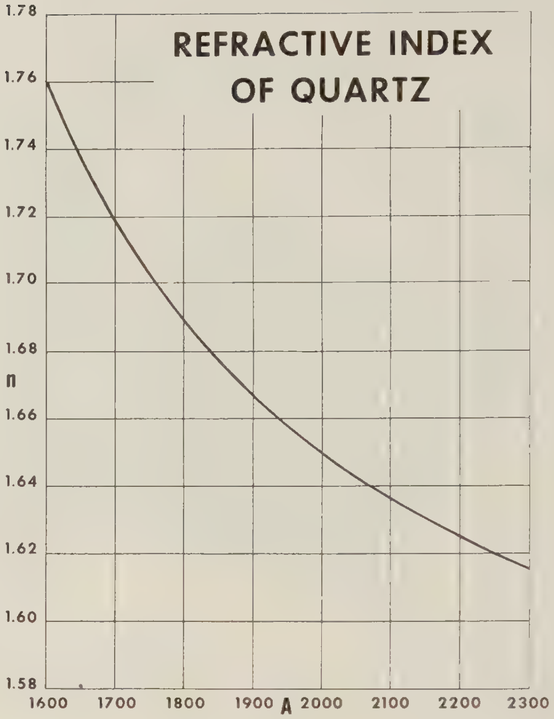

Fig. 3. Refractive Index of Quartz

A good prism must not only possess suitable transmittance, but it must also be optically homogeneous. Mechanical strains and twinning will result in poor resolution at all wavelengths. Inclusions result in scattering of light.

The far uv DK instruments are linear in wavelength presentation. In order to provide this feature the prism must be rotated non-linearly by means of a cam (scroll). The exact function for this cam depends upon the refractive index of the quartz. Careful measurements of the refractive index of the ordinary ray have been made (*8*), since early published values were found to be erroneous. The equations of Radhakrishnan have been found to be applicable to this data and serve to provide index data at intermediate wavelengths (*9*). Figure 3 is a graph of the refractive index, and Figure 4 the dispersion of quartz in the far ultraviolet region.

Detector

The detector used in this instrument is an RCA photomultiplier No. 7200. It differs from the 1P28 photomultiplier only in having a Suprasil envelope. The graded seals necessary for use of the Suprasil require that the tube be longer than the 1P28 detector. The 7200 detector responds to radiation as far as 1590 A. The absolute sensitivity of this detector below 2000 A is not known, but it is considerably superior to other detectors such as the sodium salicylate, fluorescent detectors. Solar blind phototubes such as the one used by Hansen and Buell are less

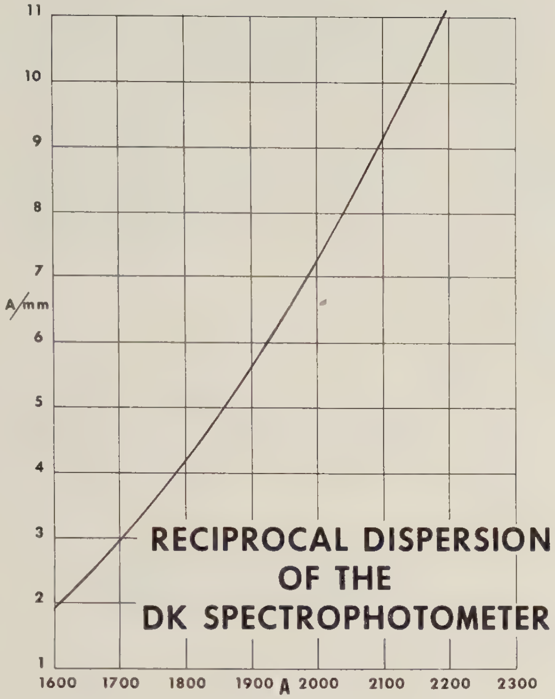

Fig. 4. Dispersion Curve

sensitive but can be used to reduce stray light at certain wavelengths (*10*). However, the 7200 tube has the tremendous advantage of response at all wavelengths from 1590 to 7500 A.

Mirrors

There are eight reflections of the primary radiation in the DK spectrophotometers. Unfortunately, the reflectivity of all useable materials decreases with decreasing wavelength. Hass and Tousey have studied the reflectivity of various materials in the far ultraviolet region (*11*). Their results show that rapidly evaporated pure aluminum overcoated with MgF_2 is the best reflector for wavelengths longer than 1600 A. Mirrors currently used in the far uv DK instruments are produced in the manner described by Hass and Tousey. The reflectivity at 1600 A is approximately 82%. When raised to the eighth power, it is apparent that about 20% of the radiation passes to the detector because of mirror reflectance factors alone. All of the spectra shown in this paper except Figure 1 were taken with an instrument whose mirrors were over one year old and were not coated with MgF_2.

It is essential that the aluminum mirrors not be exposed to corrosive gases or vapors, which might condense on the mirrors. Fortunately, the nitrogen purge used can minimize this problem. The problem of eliminating dust is not quite so easily solved. There need be no problem from dust arising from purging provided the connecting tubing between the purge gas supply and the instrument is dust free. However with time dust will accumulate on the rotating mirrors in the sample compartment and may cause a mismatch of the sample and reference beams. These and other mirror surfaces may be readily cleaned without removing the mirrors from their mounts by the method first suggested by Purcell (*12*). Allow a solution of collodion to flow over and harden on the mirror surface. After 3-5 min, cover the collodion with Scotch tape and strip. The collodion solution should be fairly viscous and should be stripped before it is completely "dry." The collodion should be unplasticized.

Purging

Oxygen and water vapor absorb far ultraviolet light and must be eliminated from the optical path in order to scan below 1950 A (*13*). Many other gases than these can cause absorption of light at even longer wavelengths. A common reason for high stray light in standard DU and DK spectrophotometers is attributable to vapors from absorbing samples and solvents lurking in the optical path long after these materials have been removed from the cell holder. Purging is recommended not only for far ultraviolet studies but also near ultraviolet and near infrared work, since it removes any solvent vapors that may escape into the optical path.

Any transparent gas may be used for purging. Nitrogen is the most readily available and least expensive gas. Hydrogen, helium, and argon have all been used successfully in the author's laboratory. Hydrogen cannot be recommended because of the explosive hazard. The moisture content of gases emerging from a cylinder is a function of the pressure in the cylinder. Water-pumped nitrogen can be used if the cylinder pressure exceeds 500 lb. Lower pressures can be used if the gas is first passed through a cartridge of molecular sieve absorbent. The author has found the AR-3 liquid nitrogen tanks supplied by Air Reduction Co.* to be most suitable. These tanks supply 2380 cu ft of nitrogen at atmospheric pressure. The oxygen and water vapor concentration in the gas has been found acceptable without further treatment. The cost of nitrogen/cu ft in these tanks is no greater than in the conventional high pressure cylinders.

The instrument is calibrated for use of nitrogen. When other gases are used having an appreciably different refractive index, one may observe a slight wavelength displacement.

The oxygen content of the purge gas must be less than 100 and preferably less than 10 ppm. The oxygen content of the purge gas can be readily determined by scanning the energy spectrum (single-beam) of the purged DK instrument in the region, 1790-1820 A. Using a slit width of approximately 0.04 mm and a slow scanning speed, a 1% absorption of the 1803.7 A band above the background energy corresponds to about 20 ppm of oxygen. As a rule nitrogen containing 100 ppm of oxygen is suitable for purging when scanning down to 1700 A. The purge gas used for operation to 1600 A should not contain over 10 ppm of oxygen. In the author's experience about 95% of the commercial water pumped nitrogen has been found to contain less than 20 ppm of oxygen. However, tanks have occasionally been found to contain around 1% oxygen and, of course, are completely unsuitable.

The DK spectrophotometer was not designed for evacuation; hence purging is the only practical way of obtaining a transparent instrument atmosphere. Even though the far ultraviolet models are sealed as well as possible they require a fairly large flow of purge gas. Figure 5 shows the effect of purge rate on the energy spectrum from 1700 to 1950 A. The oxygen bands disappear at about 1 cu ft/min of nitrogen flow. Further increase of flow rate apparently improves the transmittance of the instrument by effectively removing the water vapor that is degassing from all the internal parts of the instrument. This water vapor has a nondiscrete but intense absorption spectrum. The absorption coefficient of water reaches a maximum of 120 cm^{-1} at about 1650 A (*14*). If the instrument is maintained under a constant purge, the desorption of water vapor becomes less of a problem.

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*150 E. 2nd St., New York 17, N. Y.

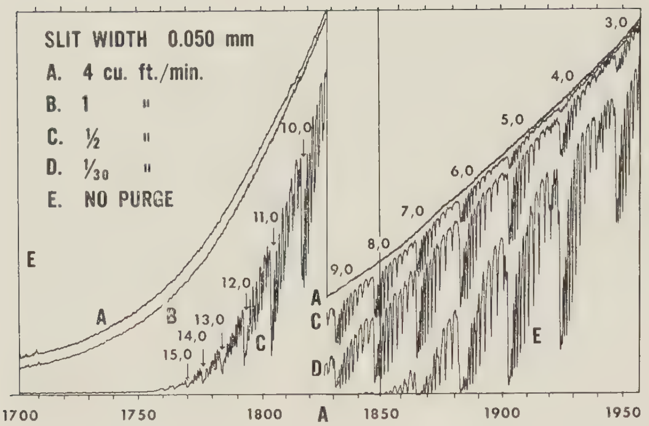

FIG. 5. EFFECT OF PURGE RATE ON SINGLE BEAM ENERGY
Nitrogen used

Slit Curvature

The theoretically desired curvature of the slits on the DK spectrophotometer varies with wavelength. Until recently all the slits on DU and DK instruments had a slit curvature of 27.9 in., which is optimum for 8000 A. However, it has been found that a 24.0 in. radius of curvature provides a better compromise. This curvature is optimum for 3000 A. Since resolution is diffraction limited at wavelengths longer than 4500 A, there is no appreciable loss in resolution by using the 24 in. radius and an increase in resolution at wavelengths shorter than 4000 A. In a region around 4000 A and below 2500 A resolution may be improved by reducing slit height provided sufficient energy is available to utilize a slit width of less than 0.05 mm.

Scanning Speed

Two factors have aggravated the problem of providing appropriate scanning controls for the far uv instruments. The high dispersion of quartz has resulted in high resolution, which in turn requires a slower scanning speed. At the same time the prism arm is required to move through a much larger angle. The most satisfactory compromise has led to the extension of the linear wavelength scroll. However, because of the change in dispersion with wavelength, it is not possible to get as many turns on the linear wavelength scrolls as on the non-linear scroll. The scanning speed on the linear wavelength instruments averages 2½ times that of the non-linear instruments.

The procedure for determining scanning speed is not widely known. Of course, it is possible to scan at a series of different speeds choosing the optimum one, but this can be very wasteful of time. It must be recognized that the optimum scanning speed is determined by both the absorption characteristics of the sample and the response of the instrument. Optimum scanning speed is defined as the maximum rate of scan that will permit the recording pen to follow the "true" spectrum to a given accuracy. This problem has been analyzed at length by Brodersen (*15*). The account given here is a simplified approximation that suffices for most purposes.

Noise is an ever present factor in high resolution spectroscopy and is always compromised with either time or resolution. Noise is reduced by either reducing instrument gain with a consequent proportional loss in resolution or by increasing the period or integration time. In the latter case the period must be increased as the square of the desired noise reduction. As a result of integration the recording pen will always lag behind the electrical signal before the integration network. When traversing an absorption band, the pen may receive a signal to reverse direction before reaching the true maximum (or minimum) position. Errors introduced in this manner can be surprisingly large.

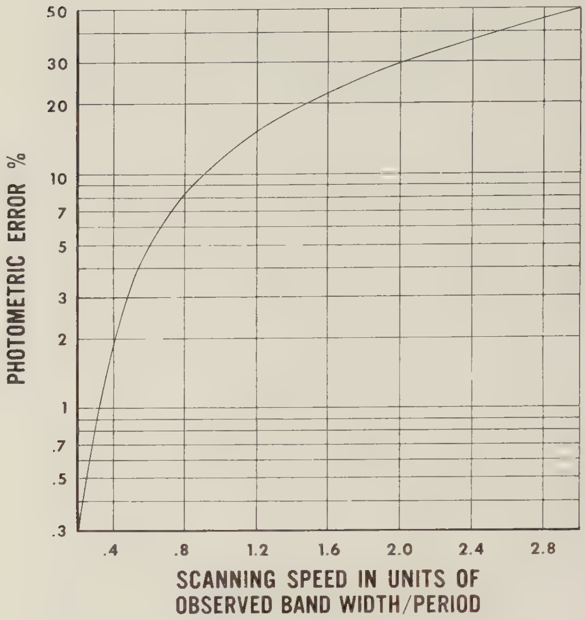

FIG. 6. EFFECT OF SCANNING SPEED

Figure 6 shows the approximate photometric error to be expected versus scanning speed. The scanning speed is given in units of observed band width per period. When working with gases possessing very sharp absorption bands, the observed band width is equal to the resolution of the spectrophotometer. In the case of liquids possessing broad bands the observed band width is equivalent to the half band width of the sample. Thus if the observed band width is 4 A, and the period is two sec, Figure 6 shows the photometric error in measuring peak absorption to be expected on scanning at various fractions and multiples of 2 A/sec. At a scan rate of 1 A/sec (one-half the observed band width/period) the photometric error due to tracking alone would be 3%. It is necessary to scan at a rate of $0.3 \times 0.6/2.0 = 0.09$ A/sec = 5.4 A/min to achieve a photometric accuracy of 1% at the maximum resolution of the instrument under the conditions used for Figure 8.

The 0.2 position of the time constant dial of the instrument is approximately equivalent to a period of 2 sec since the recorder does not quite follow an exponential trace. For purposes of these calculations the periods corresponding to the labeled time constants are given in Table I.

TABLE I. TIME CONSTANT DIAL AND PERIOD OF DK2

Time Constant Dial	*Period, Sec*
0.1	1.5
0.2	2.0
0.6	4.0
2.0	11.0

The scanning speed control of the DK-2 instrument is given in units of min per revolution of the wavelength scroll. In the ultraviolet region one revolution of the linear wavelength scroll corresponds to 1800 A. The slowest scan is 100 min/1800 A or 18 A/min. When scanning the far ultraviolet spectra of gases possessing complicated structure, this scanning speed is too fast for even the fastest response time (0.1) of the instrument. The minimum scanning speed of the DK-1 is nearly the same as the DK-2.

Several solutions to this problem exist. A drive motor with a greater gear reduction can be used on both DK-1 and DK-2 instruments. However this solution has the drawback of reducing the maximum available speed. The most convenient solution on the DK-2 is to use the time drive accessory (Beckman No. 92430). This accessory can be obtained with a number of different speed drive motors. The standard pair of motors (1/5 and 1/20 rpm) provides scanning speeds of 0.052 and 0.012 A/sec when using gears for maximum chart expansion. The scanning speeds are dependent upon the scale expansion gears, and faster speeds are obtainable with more compressed scales. Another solution preferred by the author is an electronic speed control for the standard DK-2 drive motor. It allows a continuous adjustment of scanning speed from the standard maximum speed to a minimum of 0.025 A/sec by simple adjustment of a potentiometer. A switch allows ready engagement of the standard step speed control. With this control the scanning speeds are not functions of the scale expansion gears. Scanning speed can be changed during a scan without introducing transients into the record.

Performance

Resolution

Dispersion in a Littrow mounting is related to the refractive index, n, of quartz (relative to nitrogen) and the focal length, R, of the collimator by the equation:

$$D = (9.92\sqrt{1 - (n/1.985)^2}/R)\ d\lambda/dn.$$

This equation is plotted in Figure 4 for the Beckman DK instruments where the focal length is 500 mm. For example, the *theoretical* effective band width of radiation (band width at ½ maximum intensity) passed by a slit width of 1 mm at 1600 A will be 1.9 A. However, this equation does not take into consideration the optical aberration of the instrument. By far the largest of these aberrations in the far ultraviolet region is slit curvature. By adding the values shown in Figure 7 to the instrumental slit width for a given wavelength, one can readily compute the actual resolution of the instrument.

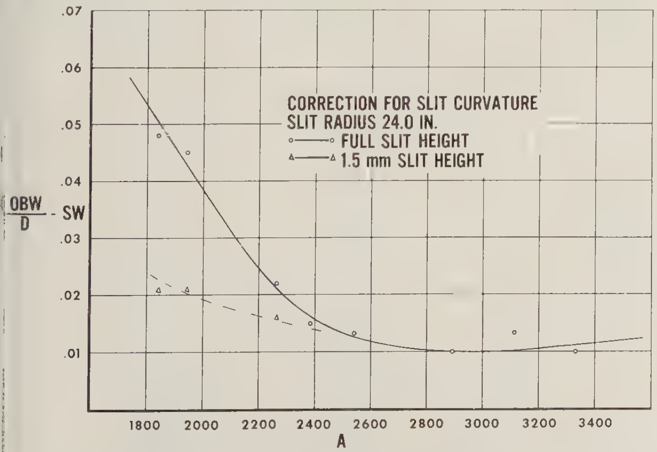

Fig. 7. Slit Curvature Correction

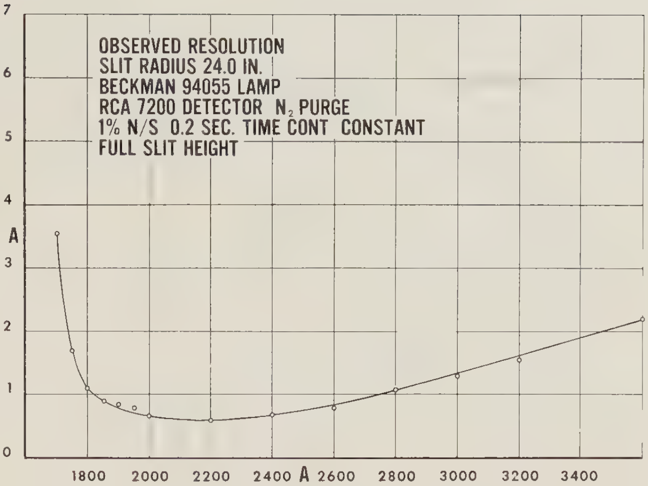

Fig. 8. Resolution Curve

It is important in making these calculations to be sure that the instrument dial is giving an accurate reading of slit width. This may be done most easily by use of the square law test. This test presumes that the light energy (displacement of the recorder pen in single beam operation) is proportional to the square of the slit width. The slit dial is usually accurate at slit widths of 0.2 mm and larger. Hence, the narrower slit readings can be calibrated for high precision work. Slit calibration is best done using light of about 3000 A.

When scanning the spectrum in double beam operation, the slit servo will automatically maintain a constant energy of radiation (as detected by the IP28) by opening or closing the slit. The exact value of slit width will be determined by the gain (sensitivity) of the amplifier. This presumably will have been set by the operator to meet his requirement of signal-to-noise ratio at a given period setting (time constant). Detectors vary considerably in sensitivity but not so much in signal-to-noise ratio. Hence instruments may vary somewhat in the gain required to produce a certain signal-to-noise ratio, but this has little to do with instrument performance. The important factor is slit width, which will yield a given signal-to-noise ratio. Figure 8 shows the actual resolution as a function of wavelength for a given set of conditions. These values have been checked using mercury vapor emission lines.

The slit width corrections and resolution achieved with the 27.9 in. radius of curvature slits has been treated in an earlier publication (*2*).

Slit jaws with a radius of curvature of 20 in. produce superior resolution in the far ultraviolet region. However, the improvement in resolution is small unless one uses narrow slit widths, and this dictates high amplifier gain. Resolution in the longer wavelength region is impaired by this short a radius of curvature for the slit. If one can use high amplifier gain, the resolution can better be improved by reducing slit height.

Stray Light

The limiting factor on wavelength range of the far ultraviolet instruments is stray light. An arbitrary specification of 0.3% maximum stray light at 1700 A has been established for these instruments (with MgF_2 overcoated mirrors). Many instruments possess considerably less stray light than this.

Stray light is defined as the ratio of undesired radiation to desired or primary radiation and is usually expressed as

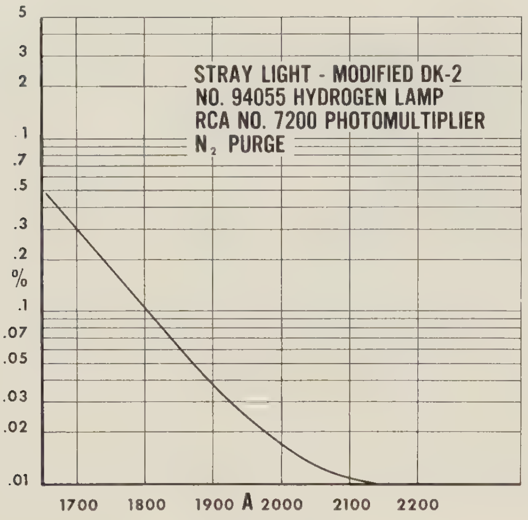

FIG. 9. STRAY LIGHT CURVE

a percentage. Undesired radiation in the ultraviolet region is defined as all radiation (passing the exit slit and affecting the detector) having a wavelength greater or less than 1.5 effective band widths from the band center. Of course the effective band width is a function of the slit width and instrument dispersion. The computation of effective band width has been shown previously. There is little value in differentiating between near and far stray light in the DK spectrophotometer in the ultraviolet region as Tunnicliff has done, although his techniques are valuable (*16*). The slit function in the ultraviolet region of the DK spectrophotometer has been found to be triangular in shape to a very close approximation (*2*). The light intensity at the base of the triangle is not zero due to stray light. One can say that the triangular slit function rests on a base of stray light. The absolute level of light scattered in the monochromator is essentially constant in the ultraviolet region. However, since stray light has been defined as a ratio it varies inversely as the intensity of the primary radiation.

It can be seen from Figures 1 and 5 that the energy of the primary radiation from the hydrogen lamp decreases with decreasing wavelength until the discrete emission lines are encountered. The stray light (ratio) is inversely proportional to intensity of the primary radiation. As a result the total stray light at various wavelengths follows the curve shown in Figure 9.

The magnitude and spectral distribution of stray light at various wavelengths of primary radiation can be determined using such spectra as are given in Figure 10. The assumption is made here that most of the scattered light, when operating below 2000 A, will arise from radiation of wavelength longer than the cut off wavelength of the filter used. This is logical in view of the rapid rise in intensity (as detected) with wavelength. It has been confirmed by using the sharp 1849 A absorption band of mercury in a manner similar to that used by Tunnicliff (*16*). In order to use sharp cut off solutions for checking stray light at wavelengths above 1800 A, it is necessary to place neutral density screens in the reference path of the instrument.

The sources of light scattering have been studied extensively. In a dust free instrument the major portion of scattered light arises from imperfections of the prism and collimator. When conditions permit it may be further reduced by decreasing slit height and placing an aperture at the image of the prism in the exit optics.

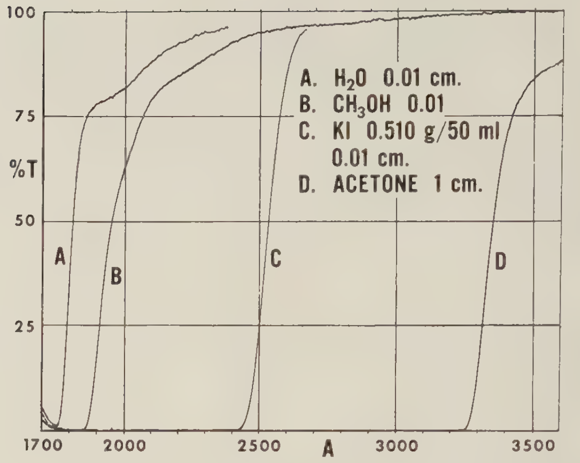

FIG. 10. SPECTRA OF SAMPLES FOR STRAY LIGHT TEST

Wavelength Calibration

The oxygen absorption bands provide an ideal wavelength calibration tool for the region from 1760 to 2000 A. The wavelengths of the Schumann-Runge bands have been determined accurately. The work of Curry and Herzberg is best for the low vibrational quantum number lines between 1920 and 2000 A (*17*). Knauss and Ballard have covered adequately the intermediate lines between 1760 and 1925 A (*18*), while Brix and Herzberg have recently studied the lines to the 21-0 band at 1750 A (*19*). Table II identifies the band heads of these bands; they are identified in Figure 5.

Another very useful calibrating material is mercury vapor. The resonance line at 1849.6 A is very sharp and intensely absorbing at room temperature. A drop of mercury in a one cm cell that has been purged with nitrogen or argon will provide good absorption. The line is so sharp its intensity will, of course, be a function of slit width. The resonance line at 2536 A can also be used for wavelength calibration; however a 10 cm cell should be used.

For shorter wavelengths the discrete emission lines of the hydrogen lamp may be used. References to these emission lines have already been cited. The weak but useable lines superimposed on the continuum around 1711 A do not seem to have been studied before.

In order to scan below 1700 A it is necessary to offset the collimator with the wavelength adjustment screw at the left end of the monochromator. This adjustment may require readjustment of the diagonal mirror immediately in front of the entrance slit. It should be adjusted for

TABLE II. WAVELENGTHS OF OXYGEN ABSORPTION BAND HEADS (VACUUM)

Band	*Wavelength, A*	*Wavenumber, cm^{-1}*
1-0	1998.2	50044.6
2-0	1972.4	50708.9
3-0	1947.4	51351.1
4-0	1924.1	51972.3
5-0	1902.6	52560.2
6-0	1882.3	53125.4
7-0	1863.6	53660.1
8-0	1846.4	54160.0
9-0	1830.7	54625.1
10-0	1816.4	55053.4
11-0	1803.7	55441.6
12-0	1792.6	55785.8
13-0	1783.0	56085.8
14-0	1774.9	56340.5
15-0	1768.3	56550.3

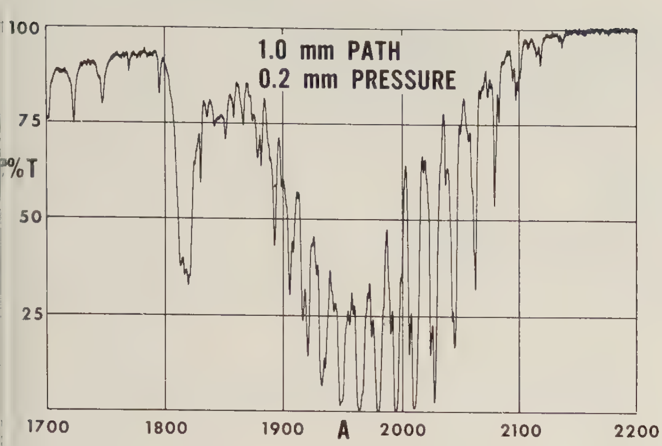

Fig. 11. Spectrum of CS$_2$ Vapor

maximum energy. When repositioning the collimator so that the wavelength dial reads correctly, it is important that an emission line in the visible be used as a small error in the far ultraviolet may produce a very large error in the visible. The 6562.8 A band of the hydrogen emission is recommended for this purpose. It is easily recognized as the longest wavelength radiation of appreciable intensity from the hydrogen lamp.

100% Level

Difficulties are seldom encountered in getting new instruments to draw a flat 100% line within ±1%. This is easily checked by drawing a double beam trace with no cells in either beam. If difficulties are encountered on aging of mirrors, the collodion cleaning technique usually restores proper operation. When sample and reference cells are used, it is not easy to balance the beams throughout the useable far uv region. Cell windows are contaminated quite easily. They may be cleaned with methanol and lint free tissue.

When the spectra of pure liquids are being obtained, it is desirable to place a single silica plate in the reference beam. The major cell losses are due to reflection from the air-silica interfaces. Curve A of Figure 2 shows the magnitude of these reflection losses. For accurate work the thickness of silica in the two paths must be equal. The transmittance of the suprasil used for special far ultraviolet cells usually exceeds 95% for 1 mm thickness at 1700 A after correction for reflectance loss.

Figure 11 demonstrates the overall performance of the instrument in tracing automatically the relative transmittance spectrum of carbon disulfide vapor. The superposition of vibrational and electronic states is quite evident. This spectrum has been analyzed by Price and Simpson *(15)*. The absorption bands are extremely intense as evidenced by the low pressure and short optical path used. A large number of organic and inorganic gases possess very discrete spectra in the region described here. It is likely that these spectra will find wide use in analysis and molecular structure studies.

Acknowledgment

The author is indebted to Mr. B. D. Henderson and Mr. J. McDaniel for assistance in this work.

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Infrared Spectra of Vitamins, a Schiff Base, and an Amino Acid Chelate in Water

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Abstract

The infrared spectra of some vitamins in water are presented. The spectra of two forms of vitamin B_6 are included and that of the Schiff base formed between pyridoxal phosphate and glycine. The spectrum of copper (L-lysine)$_2$ is given as an example of an amino acid chelate compound in water.

Introduction

The application of infrared spectroscopy to aqueous solutions has been growing very rapidly. Reviews by Blout (*1*), Nachod and Martini (*2*) and by Goulden (*3*) attest to this fact. In the interest of extending the uses of infrared spectroscopy to a wider variety of substances of biochemical interest the spectra of some vitamins and related compounds in the range 6.1 to 11.0 μ are reported in this paper. Rosenkrantz (*4*) has published a review of the spectra of vitamins in the solid state. Many of these compounds are soluble only in water, and thus the only choice for determining their infrared spectra lies between water and solid state work. Solid state spectra are often unsatisfactory because bands due to the crystalline state of the materials are seen and can be confused with fundamental vibrational frequencies.

Reagents

The vitamins were obtained from the following sources: calcium pantothenate (Mann Laboratories, M. A.), thiamine hydrochloride (Fisher Scientific Co.), pyridoxine hydrochloride (Fisher), nicotinamide (Eastman), and choline chloride (General Biochemicals, Inc.). The sodium pyridoxal phosphate was prepared by Mr. Frederick Dorer according to the methods of Peterson, *et al.* (*5*). The copper(lysine)$_2$ was prepared by the method of Kurtz (*6*) and was a gift from Dr. Donald M. Kirschenbaum. Glycine was purchased from Mann Research Laboratories and was their M. A. product.

Apparatus and Techniques

The vitamin spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer for solutions contained in a BaF_2 cell. Cell thicknesses and concentrations of solutions are indicated in the legends. A transmittance screen was used in the reference beam essentially as described previously (*7, 21*). Occasionally, two BaF_2 plates with a polyethylene spacer (0.032 mm) were used instead of the manufactured BaF_2 cell in the sample beam.

Results and Discussion

Figure 1 shows the spectra of water and of calcium pantothenate. It can be seen that this vitamin shows fewer bands in water in the region examined than in the solid state (*4*) (Figure 1a), and the bands are also broader. That fewer bands generally appear in water solutions has been noted by other investigators too. There is little correspondence between the spectra of the vitamins in the solid state and in water.

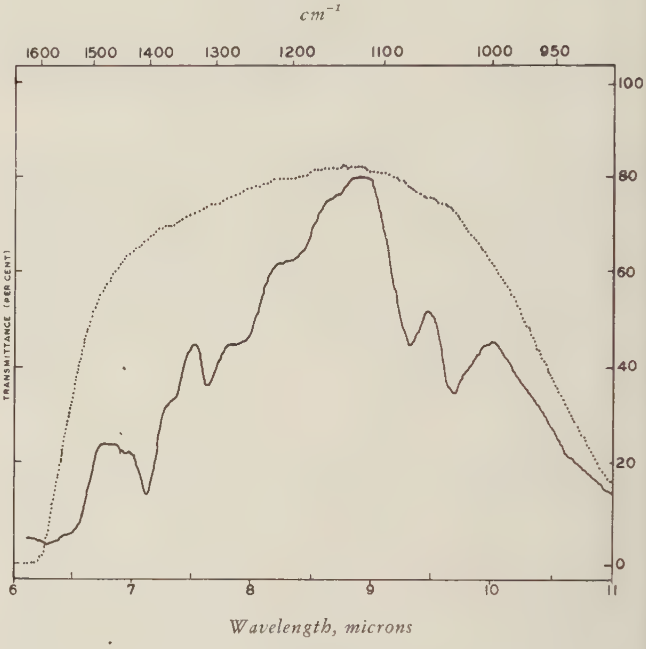

FIG. 1

.... DISTILLED WATER, —— CALCIUM PANTOTHENATE, 10% SOLUTION IN 0.053 MM, BaF_2 CELL VS. TRANSMITTANCE SCREEN

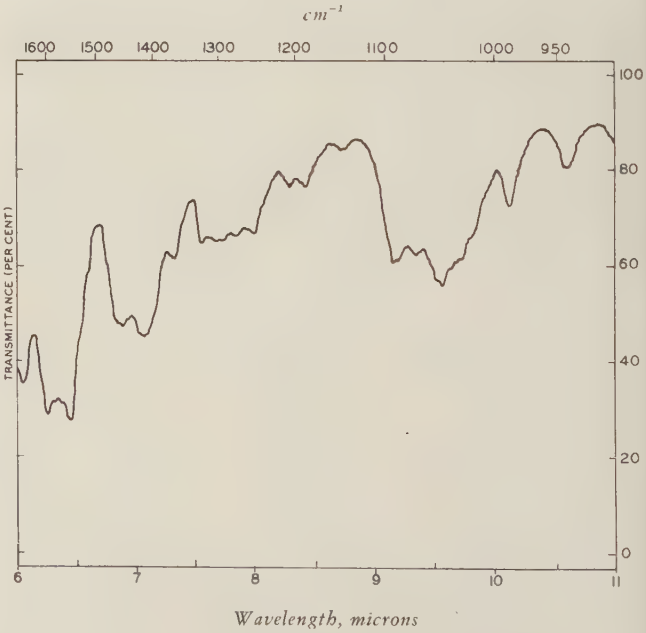

FIG. 1a

—— CALCIUM PANTOTHENATE IN KBR PELLET

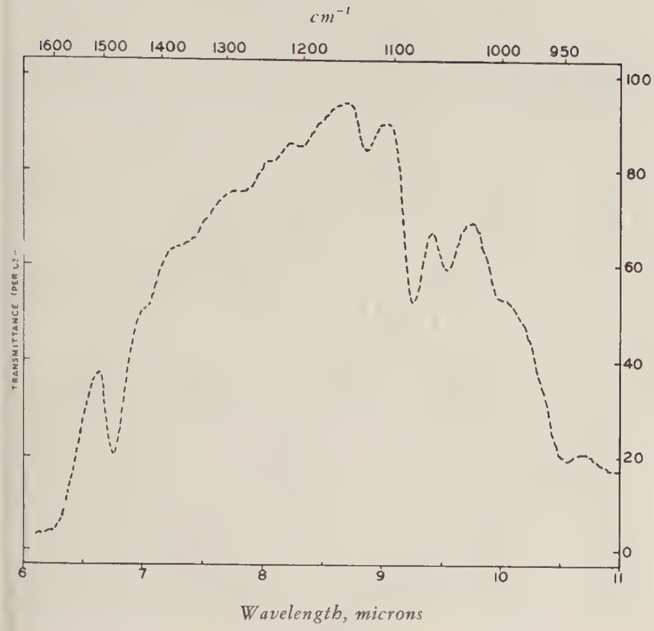

FIG. 2

----- CHOLINE CHLORIDE, 10% SOLUTION IN 0.053 MM, BaF$_2$ CELL VS. TRANSMITTANCE SCREEN

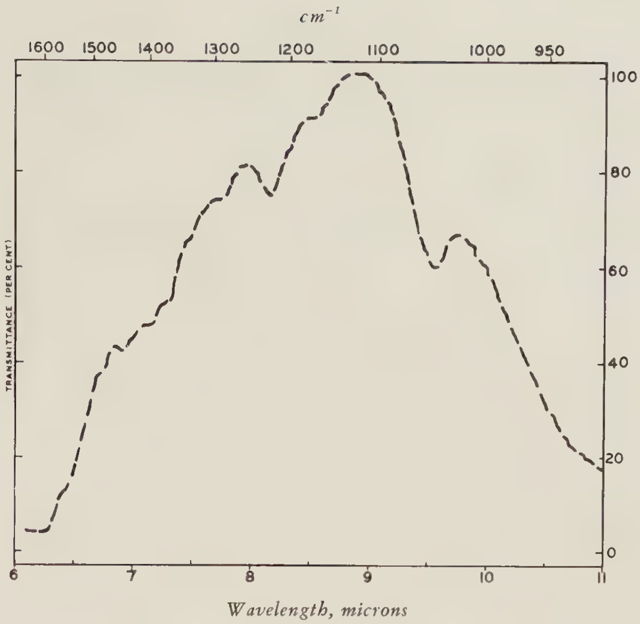

FIG. 3

----- THIAMINE·HCL, 10% SOLUTION IN 0.053 MM, BaF$_2$ CELL VS. TRANSMITTANCE SCREEN

Figure 2 shows the spectrum of choline chloride. It is of interest to point out that Raman spectral data in the same region of the spectrum agree rather well with those found in the infrared for this compound. In Table I the values determined by Edsall (*8*) using Raman techniques are compared with the infrared values.

The spectrum of thiamine.HCl is given in Figure 3.

Nicotinamide is an essential chemical part of certain coenzymes and therefore its spectrum, which appears in Figure 4, may be of especial interest.

Figure 5 shows the spectrum of pyridoxine·HCl. Again the bands do not correspond well with those found in the solid state. Pyridoxal phosphate is an essential part of transaminase systems (*9*), and chelate compounds involving a Schiff base have been postulated to be a means of transporting amino acids across cellular membranes (*10*). Therefore, it is felt that spectra of such compounds in water may be useful in biochemical studies. Figure 6 shows three spectra: (a) phosphate buffer, pH 7.3, ionic strength 0.05, (b) pyridoxal phosphate sodium salt, dissolved in that buffer (0.03 g/5.00 ml of buffer), and (c) the Schiff base formed between sodium pyridoxal phosphate (0.03 g) and glycine (0.0084 g) in 5.00 ml of the buffer (*11,12*). No values are given for the % transmittance in order to put three spectra in the same figure. The fact that the buffer itself (at the given concentration) has only one band would seem to make it quite useful for studying biochemical systems. Figure 7 shows the spectrum of the amino acid, glycine.

TABLE I. RAMAN AND INFRARED BANDS OF CHOLINE CHLORIDE, CM^{-1} [a]

Raman	*Infrared*
955	948
1009	1004
1058	1048
1089	1080
1142	1129
1209	1200
1239	1239
1278	1279
1342	1348
1450	1425
1478	1479

The spectrum of Cu(L-lysine)$_2$ an amino acid chelate, appears in Figure 8. For comparison the spectrum of DL-lysine•HCl is given in the same figure. The ordinate values refer to DL-lysine·HCl. DL-lysine·HCl and L-lysine produce spectra almost identical to each other in water in saturated solutions which have been compared (*18*). The identicalness is real and not due to lack of signal in the 8-10 μ region. Pen response was checked even in the poor signal regions.

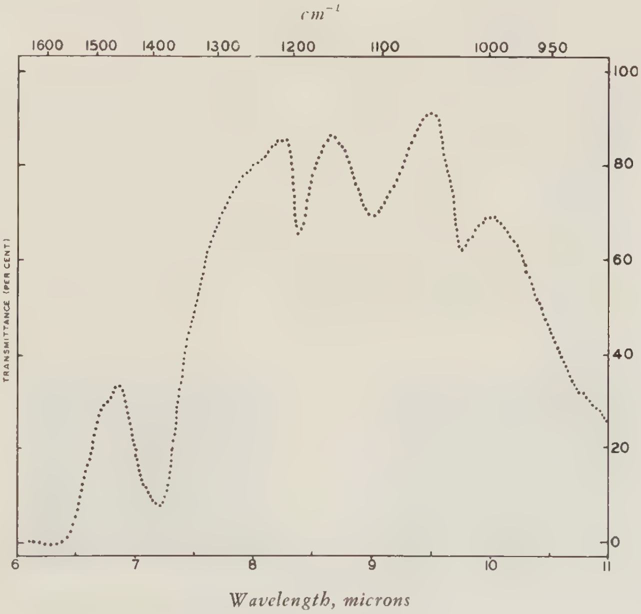

FIG. 4

.... NICOTINAMIDE, 20% SOLUTION IN 0.049 MM, BaF$_2$ CELL VS. TRANSMITTANCE SCREEN

---

[a] From (*8*)

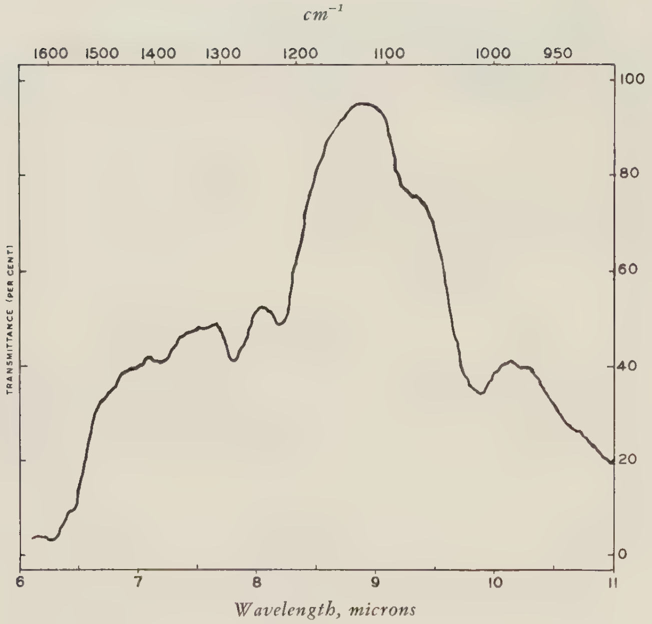

FIG. 5

—— PYRIDOXINE•HCL, 9.2% SOLUTION IN 0.053 MM, BaF_2 CELL VS. TRANSMITTANCE SCREEN

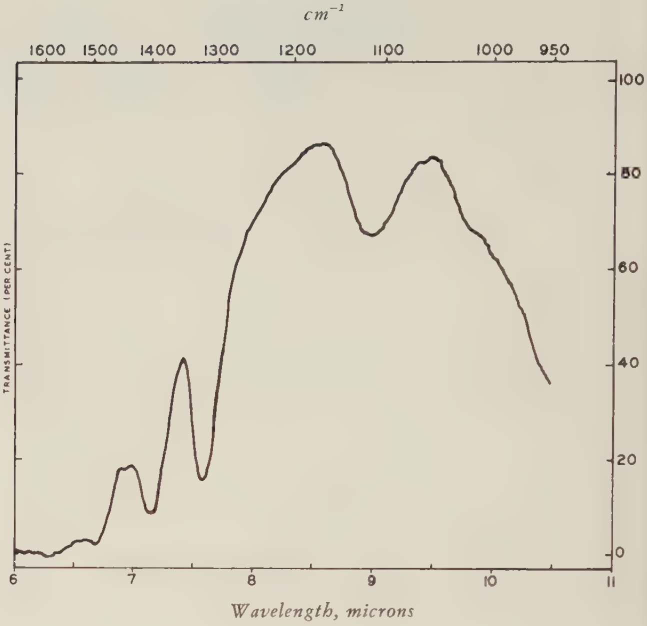

FIG. 7

—— GLYCINE 7.5% SOLUTION IN 0.049 MM, BaF_2 CELL VS. TRANSMITTANCE SCREEN

There are many structure problems which lend themselves to the application of aqueous infrared spectroscopy. Gore, *et al.* (*13*), have presented spectra of certain amino acids. Blout (1) has studied biological materials of high molecular weight in water and D_2O. Miles (*14*) has investigated polynucleotide interactions, and Susi, *et al.* (*15*), have investigated the carboxyl ionization of β-lactoglobulin. Spectra concerning the hydrolysis of a thiazolidine compound (*16*), the dissociation of phenol to phenoxide ion (*17*), various amino acids (*18,19*), the mutarotation of glucose and of mannose (*20*), and spectra of other compounds (*21*) of biochemical interest have been reported by our laboratory. Obviously, to demonstrate certain phenomena, water is the solvent of choice and these phenomena are easily observed with infrared spectroscopy.

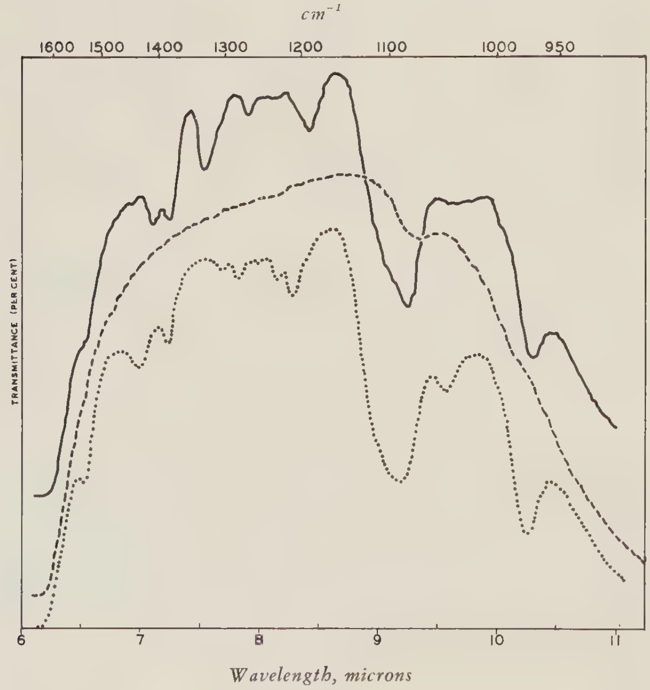

FIG. 6

----- PHOSPHATE BUFFER, pH 7.3, IONIC STRENGTH 0.05
.... PYRIDOXAL PHOSPHATE (SODIUM SALT), 0.03 G DISSOLVED IN 5.00 ML OF THE BUFFER
—— SCHIFF BASE FORMED BETWEEN 0.03 G OF SODIUM PYRIDOXAL PHOSPHATE AND 0.0084 G OF GLYCINE IN 5.00 ML OF THE BUFFER.
All three solutions in 0.032 mm, BaF_2 cell vs. transmittance screen.

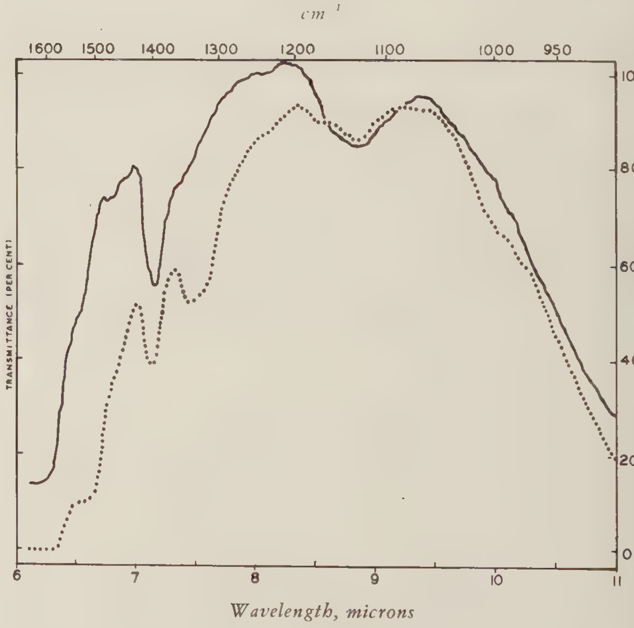

FIG. 8

—— Cu(L-LYSINE)$_2$, 10% SOLUTION IN 0.0227 MM, BaF_2 CELL VS. TRANSMITTANCE SCREEN
.... DL-LYSINE·HCL, 10% SOLUTION IN 0.025 MM, BaF_2 CELL VS. TRANSMITTANCE SCREEN

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Minimizing Matrix Effects in Stainless Steel, Type 422, Using Oxygen in the Analytical Gap

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Abstract

A routine emission spectrographic procedure has been developed for the analysis of stainless steel, Type 422, using the point-to-plane technique. By directing a stream of oxygen onto the face of the sample the accuracy and reproducibility were made better than that obtained in an atmosphere of air.

Introduction

In the development of a routine emission spectrographic method for the analysis of Type 422 stainless steel, various samples gave very erratic results. In conjunction with these results there was a very definite variation in the physical appearance of the spark craters. An investigation was begun to find the cause of this condition and also to develop a method to overcome it, using the point-to-plane technique.

Metallographic Investigation

Pieces were cut from various samples which gave erratic results and showed variations in the spark craters. These pieces were identified as *A*. Pieces were also cut from samples, which gave consistent results and uniform spark craters. These pieces were identified as *B*. The microstructures were examined, and it was noted that all samples marked *A* were the same and all samples marked *B* were the same. However, the microstructure of the two groups differed as shown in Figure 1.

Procedure

The basic procedure for conventional spark excitation was employed, using the Jaco-Varisource. Spectrograph, excitation conditions, microphotometer, line pairs, and photographic procedure are given in Table I. Calculations were made using the "Atomic Dilution Factor" (*1*). The samples were machined to a flat surface and finished on an 80-grit aluminum oxide belt.

Atmosphere

It was noted that in the examination of the spectra, the Fe lines used as the internal standard lines were very light in sample *A*, but were of normal density in sample *B*. Since an improvement in reproducibility has previously been reported for a nickel base alloy (*2*) by blowing nitrogen on the sample during sparking and also a reduction of matrix effects (*3*) by using a mixture of gases, these methods were tried. But is was found that a stream of oxygen gave the most reproducible results. A small glass tube was constructed with an opening of 2 mm. This tube

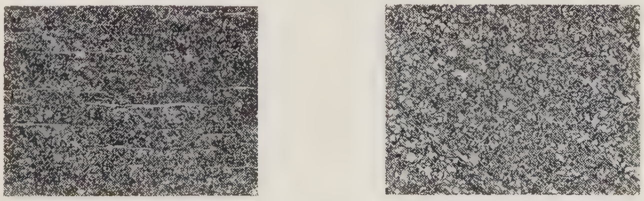

Fig. 1. Photomicrographs of Samples of Type 422 Stainless Steel Showing Two Microstructures Observed

Left—Sample A, Right—Sample B, Magnification—40X, Etchant—Grard No. 2

TABLE I. SPECTROGRAPHIC AND PHOTOGRAPHIC CONDITIONS

SPECTROGRAPH AND ACCESSORIES

Spectrograph	3.4 m Jarrell-Ash
Grating	15,000 lines/in.
Dispersion	2.5 A/mm in 2nd order
Slit Width, μ	15
Slith Height, mm	2

EXCITATION

Source	Jarrell-Ash Varisource
Analytical Gap	2 mm
Inductance	Residual
Capacitance	0.0075 mfd
Resistance	1 ohm
R.F. Amps.	9.5
Breaks/Half-Cycle	5
Preburn	10 sec
Exposure	24 sec
Oxygen Flow	1 l/min

LINE PAIRS

Element	*Int. Std. Line, Fe*	*Element Line*	*Range, %*
Si	2868A	2881A	0.10- 1.00
Mn	2805A	2886A	0.30- 2.00
V	2805A	2904A	0.15- 0.60
Cr	3011A	3013A	10.00-15.00
Ni	3011A	3012A	0.15- 3.00
Mo	2805A	2775A	0.10- 1.30

All work was performed in the second order.

PHOTOGRAPHY

SA-1 Emulsion
D-19 Developer 2 min
Short Stop—15 sec—5% Acetic Acid
Fixer—3 min, Kodak Acid Fixer
Entire procedure carried out at 20°C

MICROPHOTOMETER

Jarrell-Ash Non-Recording
Slit Dimension—1.5 mm x 10 μ

was attached to a length of rubber tubing and fastened to the bottom electrode holder. It was placed so that the top of the glass tube was just below the point of the hemispheriacally tipped counter electrode, and the oxygen was blown directly on the face of the sample. The flow of oxygen was controlled by a multi-stage regulator†. Various flows were tried, from 5 l/min to ½ l/min. The spark craters were examined and also the Fe and element lines of the spectra. It was found that a flow of 1 l/min was satisfactory. When flows of less than 1 l/min were used the variations occurred to some degree, and when flows of more than 1 l/min were used there was a definite flaring of the spark discharge. This gave erratic density readings of the internal Fe lines and also the element lines. Air (*4*) was also tried as an atmosphere but no great improvement was noted. Figure 2 shows the spark craters of sample *A* and *B* both with a stream of oxygen on the face of the samples and without the oxygen on the face of the samples.

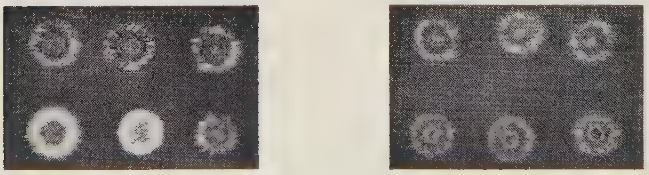

FIG. 2. APPEARANCE OF BURNS IN OXYGEN (TOP) AND IN AIR (BOTTOM)

Left—Sample A, Right—Sample B

TABLE II. ANALYTICAL DATA FOR SAMPLES WITH ERRATIC RESULTS IN AIR AND VARIATION IN SPARK CRATERS

Sample	*Element*	*Chem. Anal., %*	*Atm.*	*Spec. Anal., %*	*Coeff. of Var., %*[a]
A-1	Mo	0.95	Air	0.92	11.7
			O_2	0.96	1.6
	Mn	0.74	Air	1.01	21.3
			O_2	0.73	0.9
	V	0.26	Air	0.48	9.9
			O_2	0.27	0.6
	Cr	12.79	Air	13.33	6.6
			O_2	12.87	3.6
	Ni	0.80	Air	0.76	3.7
			O_2	0.79	1.6
	Si	0.70	Air	0.84	11.2
			O_2	0.69	1.6
A-2	Mo	1.00	Air	0.90	5.8
			O_2	1.00	1.3
	Mn	0.78	Air	1.31	25.3
			O_2	0.76	1.4
	V	0.25	Air	0.40	17.5
			O_2	0.25	0.5
	Cr	12.76	Air	13.77	4.1
			O_2	12.77	1.3
	Ni	0.80	Air	0.76	3.4
			O_2	0.81	1.8
	Si	0.72	Air	0.74	11.8
			O_2	0.70	1.2
A-3	Mo	0.84	Air	0.75	5.8
			O_2	0.85	1.1
	Mn	0.58	Air	1.23	14.5
			O_2	0.57	2.0
	V	0.28	Air	0.61	11.1
			O_2	0.28	0.5
	Cr	12.78	Air	13.62	5.1
			O_2	12.73	0.9
	Ni	0.80	Air	0.75	2.8
			O_2	0.80	0.4
	Si	0.53	Air	0.80	14.0
			O_2	0.53	1.3
A-4	Mo	0.95	Air	0.82	17.2
			O_2	0.95	1.0
	Mn	0.76	Air	1.96	22.3
			O_2	0.76	1.6
	V	0.25	Air	0.59	7.6
			O_2	0.26	0.5
	Cr	12.74	Air	14.09	8.0
			O_2	12.75	2.6
	Ni	0.82	Air	0.79	2.0
			O_2	0.81	1.5
	Si	0.76	Air	0.95	5.1
			O_2	0.75	1.6
A-5	Mo	1.01	Air	0.95	11.3
			O_2	1.00	1.4
	Mn	0.75	Air	1.25	34.1
			O_2	0.73	1.7
	V	0.27	Air	0.49	11.5
			O_2	0.27	1.0
	Cr	12.58	Air	13.16	6.8
			O_2	12.61	2.9
	Ni	0.76	Air	0.73	2.1
			O_2	0.80	0.5
	Si	0.78	Air	0.76	6.1
			O_2	0.75	1.6
A-6	Mo	1.00	Air	0.96	7.8
			O_2	1.00	1.5
	Mn	0.70	Air	1.32	20.3
			O_2	0.72	1.4
	V	0.24	Air	0.56	20.1
			O_2	0.25	1.1
	Cr	12.77	Air	13.61	8.6
			O_2	12.77	1.9
	Ni	0.85	Air	0.76	3.4
			O_2	0.81	0.9
	Si	0.81	Air	0.89	15.4
			O_2	0.80	1.2

[a] Computed from 6 exposures.

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†Harris Calorific Company

Table III. Analytical Data for Samples with Consistent Results in Air and Uniform Spark Craters

Sample	*Element*	*Chem. Anal., %*	*Atm.*	*Spec. Anal., %*	*Coeff. of Var., %*[a]
B-1	Mo	1.05	Air	1.06	1.9
			O_2	1.05	1.3
	Mn	0.81	Air	0.83	1.8
			O_2	0.83	0.8
	V	0.20	Air	0.22	1.4
			O_2	0.22	1.2
	Cr	12.28	Air	12.33	2.0
			O_2	12.32	1.4
	Ni	0.83	Air	0.83	1.6
			O_2	0.84	1.0
	Si	0.11	Air	0.16	3.7
			O_2	0.14	2.0
B-2	Mo	1.00	Air	1.00	2.1
			O_2	1.00	1.1
	Mn	0.84	Air	0.83	2.0
			O_2	0.84	1.0
	V	0.22	Air	0.23	1.9
			O_2	0.23	1.1
	Cr	12.65	Air	12.65	2.5
			O_2	12.65	1.3
	Ni	0.83	Air	0.81	1.6
			O_2	0.81	1.2
	Si	0.30	Air	0.28	2.6
			O_2	0.28	1.3
B-3	Mo	0.98	Air	0.98	1.4
			O_2	0.98	0.8
	Mn	0.80	Air	0.81	1.7
			O_2	0.80	1.0
	V	0.19	Air	0.20	1.5
			O_2	0.20	1.0
	Cr	12.26	Air	12.29	4.0
			O_2	12.26	1.2
	Ni	0.84	Air	0.83	2.1
			O_2	0.84	1.2
	Si	0.27	Air	0.25	1.2
			O_2	0.25	1.1

[a] Computed from 6 exposures.

Results and Reproducibility

All samples used in the investigation were analyzed in duplicate by wet chemical methods. Spectrographically the samples were run six times in air and six times with oxygen on the face of the sample. The results and reproducibility are given in Tables II and III. Table II shows the results of data obtained on samples *A* with and without the oxygen on the face of the samples, compared with the results from the wet chemical analyses. Table III shows the same data for samples marked *B*. There are no tungsten results reported because this element was determined by using the ac arc form of excitation, and no variation between samples *A* and *B* were observed. The ac arc form of excitation was tried for the other elements, and the reproducibility was very poor in both samples. This was especially true in the case of Cr and Mn.

Discussion

Acceptable reproducibility and results were obtained by using oxygen on the face of the sample. As to the exact reason for this improvement in reproducibility and accuracy, only an assumption can be made. It is assumed that the oxygen gives a more arc-like discharge, allowing more material to be consumed. Also the oxidizing atmosphere may have a tendency to offset the metallurgical effects. It will be noted from the results in Tables II and III that the erratic results only occur when the silicon content is above 0.35%. It is concluded from the results obtained, that this method is satisfactory for the analysis of this type of material.

Acknowledgments

The cooperation of the staff of the Metallurgical and Chemical Laboratories of the Westinghouse Electric Corp., Lester Plant, is gratefully acknowledged. The author wishes to thank Mr. N. L. Mochel and Mr. E. A. Snader, for permission to publish these results.

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The Spectrographic Determination of Molybdenum In Uranium-Molybdenum Alloys

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Abstract

Molybdenum can be determined as an alloying constituent in uranium-molybdenum alloys by the point-to-plane spark method of spectrographic analysis. The method covers a concentration range of 1 to 5% molybdenum, and the precision at the 95% confidence level is ± 7%. Time required for the analysis of one sample is about fifteen min.

Introduction

Alloys of uranium are gaining considerable popularity as fuel elements in various power reactor programs, and the producers and users of these alloys require reliable analytical methods for the determination of the added elements. Alloys of molybdenum have been of particular interest. Chemical methods are time-consuming and often unreliable, due to the low volatilization temperature of molybdenum compounds. The various universal methods of spectro-chemical analysis lack the desired precision necessary to determine if the sample meets the required specifications, and no specific references were found to deal with the spectrographic determination of molybdenum in the concentration range of interest.

The success of the point-of-plane spark method *(1)* of spectrographic analysis in the analysis of aluminum alloys, steels, and zirconium alloys *(2)*, suggested an evaluation of that method as a rapid and reliable method for the deter-

TABLE I. APPARATUS AND SPECTROGRAPHIC OPERATING CONDITIONS

Electrodes: Sample	Sample disc, ⅛ in. thick
Counter	3/16 in. hemispherical tip, U.C.P. No. 105-U
Analytical gap, mm	2
Excitation unit	Baird-Atomic
Capacitance, μfd	0.0075
Inductance, μh	6.0
Resistance, ohm	None added
Breaks/half cycle	8
Current, r.f. amp	7.0
Exposure, sec	20
Pre-exposure, sec	10
Spectrograph	Baird-Atomic, 3 m Eagle, 15,000 line/in. grating, 1st order
Wavelength range, A	To include 2450 to 3750
Slit width, μ	50
Sector holder	27.0 cm from slit
Arc stand	49.4 cm from slit
Filter	Neutral, 6% transmitting
Photographic emulsion	Eastman SA-2
Developer	Kodak D-19, 20° C, 4 min
Plate Calibration	Two-step method, iron arc exposure
Line Pairs	
Molybdenum	3871.50 A
Uranium (internal standard)	2889.62 A

mination of molybdenum in uranium-molybdenum alloys. The results of that investigation are the basis of this report.

Experimental

Neither primary nor secondary standards of uranium-molybdenum alloys were available commercially. The samples and the samples used as standards in this investigation, were discs ⅛ in. thick that were sawed out of ingots. The molybdenum content of the standards was determined chemically by a colorimetric method *(3)*. In order to obtain reliable standards, the discs used as standards were those that showed the best precision on repeat analysis by the chemical method. Several specimens were selected as standards, and these were used to prepare a spectrographic working curve; those that fell off a straight line calibration curve were discarded. From ten samples, six were selected as standards because of the precision obtained by sparking various points along the surface.

The spectrograph employed and the excitation and exposure conditions are listed in Table I. The optimum pre-exposure and exposure time were determined from moving plate studies. The times selected were based on density readings obtained and standard deviations of the intensity ratios of the line-pairs. Minimum standard deviations were obtained with the pre-exposure and exposure selected.

Better precision was realized by keeping the sample cool during excitation. Since a ⅛ in. sample, when sparked directly, overheated during the exposure, the sample was placed on a ½ in. iron block during excitation and immersed in water between exposures. A Petrey stand was found to be inconvenient to use in this method, as the samples varied considerably in both length and width. For this reason, the sample, mounted on an iron block, served as the lower electrode.

Most point-to-plane samples are prepared by sanding or machining. Because the samples were only ⅛ in. thick, it was felt that machining would result in too thin a sample. Preparation of the sample on a belt sander was attempted; however, because of the extreme flammability of uranium particles, excessive sparking occured, and this method was abandoned. The method adopted was to face the sample by hand with emery cloth in an enclosed area to prevent contamination.

TABLE II. METHOD USED FOR CORRECTING RESULTS

Std.	*Run*[a]	*Dev.*	*Run*[b]	*Dev.*	*Run*[c]	*Dev.*
3.01	2.85	−0.16	3.08	+0.07	2.90	−0.11
2.72	2.55	−0.17	2.73	+0.01	2.67	−0.05
1.60	1.45	−0.15	1.68	+0.08	1.52	−0.08
Ave.		−0.16		+0.05		−0.08

[a] Answers corrected by adding 0.16%.
[b] Answers corrected by subtracting 0.05%.
[c] Answers corrected by adding 0.08%.

Discussion

In order to improve accuracy, a new technique was used. Fourteen exposures are used on each 4″ x 10″ plate. Samples, where possible, were analyzed in groups of four. The exposures were done as follows: *Plate 1*, 4 exposures of Standard A, 4 exposures of 2 samples, and 2 exposures of Standard B; and *Plate 2*, 2 exposures of Standard B, 4 exposures of 2 samples, and 4 exposures of Standard C.

After calculating the intensity ratios, the concentrations for the three standards were obtained. The results obtained on the standards were subtracted from the known value, rather than shift the calibration curve. The deviations were added and divided by three. The average obtained was added or subtracted to the values obtained on the samples. Examples of this method are presented in Table II.

The concentration of molybdenum in the alloy required by the customer must be between 2.50 and 3.00 %. As a further means of insuring accurate results, a method was incorporated to recheck values that bordered on the precision limits. Samples were analyzed in the following manner: results of < 2.40%—not rechecked; results of 2.40 to 2.60%—reanalyzed; results 2.60 to 2.90%—not rechecked; results of 2.90 to 3.10%—reanalyzed; and results of > 3.10%—not rechecked.

The precision of the method was determined by sparking the same sample twenty-seven times (Figure 1). The absolute precision at the 95% confidence level was found to be ± 0.16 at a concentration of 2.32% molybdenum. The relative precision based on quadruplicate analysis is ± 3.6% at the 95% confidence level.

Some segregation has been found in several samples. Figure 1 illustrates a typical sample with spectrographic values obtained at various points. The section on the right-hand side of the figure represents the section taken for chemical analysis. If there is segregation in a particular sample, the chemical method would have a bias, depending upon the section from which the sample was taken.

The results obtained by chemical and spectrographic analysis indicated an apparent bias with the spectrographic results about 0.10% higher than the chemical results, on the average. The chemical analysis used on these samples was a gravimetric method; hence, low values would be obtained if the sample was heated at too high a tempera-

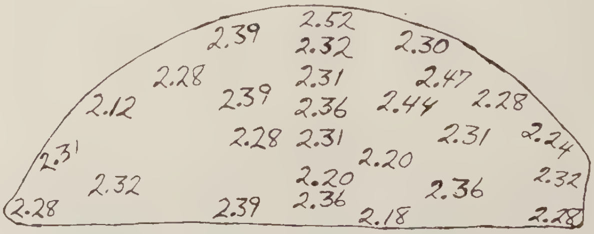

FIG. 1. TYPICAL SAMPLE SHOWING SPECTROGRAPHIC RESULTS OBTAINED AT VARIOUS POINTS

ture. In addition to the possible loss of molybdenum in the chemical method, several samples have shown some segregation, especially near the edge of the sample. Results obtained from different laboratories are listed in Table III. The spectrographic method shows a relative deviation of less than 5% compared with x-ray fluorescence.

TABLE III. COMPARISON OF RESULTS OBTAINED BETWEEN LABORATORIES

Spec.	*Lab. I X-Ray*	*Lab. I Chem.*	*Lab. II Chem.*
2.50	2.60	2.54	2.36
3.05	3.17	3.15	3.10
2.44	2.34	2.27	2.24
2.49	2.45	2.43	2.31

Background corrections were not used in this method, as this did not improve the precision. The analytical lines used are approximately 3 mm apart on the plate and the background from the uranium matrix in this region of the plate was found to be equal at both lines. The microphotometer was set at zero on background previous to reading the molybdenum line, and it was not necessary to reset the zero for the uranium line for the same exposure. Because of the background created by uranium, however, it was found to be necessary to change settings for different concentrations of molybdenum. It was believed that at the level of 99% uranium the background was too high to accurately determine the concentration of molybdenum by this method.

Conclusions

This method has proven very satisfactory from the standpoint of accuracy and speed for the determination of molybdenum in uranium-molybdenum alloys. Approximatey fifteen min are required to analyze one sample. The spectrographic results agree with results obtained by other methods, as well as chemical results obtained in different laboratories.

Acknowledgment

Acknowledgment is made to the staff of the Chemical Laboratory of the Davison Chemical Company, Nuclear Reactor Materials Plant, for their cooperation in the analysis of standards and samples.

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A Technique for Obtaining the Ultraviolet Absorption Spectrum of Solid Keratin

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Abstract

A technique is described for obtaining spectra of solid keratin in the form of thin sections of horse tail hair. The method of sectioning, mounting the specimen, and positioning it in the beam of the spectrophotometer is given. The application of a correction procedure for scattering, which has previously been described by other authors, and a corrected ultraviolet absorption spectrum of keratin are included in the report.

Introduction

Most work on the absorption spectrum of keratin, as indeed of proteins generally, is carried out in solution, because the material is not normally available in films of suitable thickness; only isolated reports have appeared in the literature on the spectrum of the solid (*1,2*). Keratin is an insoluble protein and can only be dissolved after fairly severe chemical treatment. The information that can be obtained from the protein in solution is therefore limited, and data about the actual structural environment of the chromophoric groups in the solid material cannot be obtained by this technique. Apart from avoiding these disadvantages, use of solid keratin affords the possibility of working with the material under different conditions of strain, water content, etc., as well as the application of the valuable technique of polarized radiation. This report is confined largely to a description of the experimental technique, and the important scattering correction. An absorption spectrum of unstretched keratin is included in the report. Details of further results obtained with this technique have been reported elsewhere (*3*).

Experimental

An Optica CF4 spectrophotometer was used for this work and was modified to permit the use of long, narrow specimens (Figure 1a). The beam leaving the exit slit of the monochromator was condensed by a fused silica lens, which formed an image of the filament near the specimen position. The reduction of beam cross-section from about 5 x 5 mm to about 1 x 5 mm was achieved without losing appreciable energy at the photomultiplier detector. For measurements of ultraviolet dichroism of the specimen, a commercially available polarizing prism of the Glan-Foucault type was placed between specimen and detector.

The material selected for this investigation was near-white, horse-tail hair of 200-250 μ diam. Thin longi-

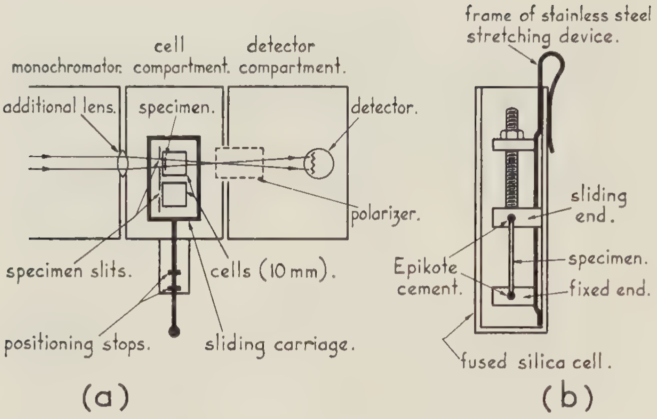

FIG. 1. (a)—DIAGRAM OF THE MODIFIED OPTICAL SYSTEM AND SPECIMEN ARRANGEMENT, (b)—METHOD OF MOUNTING HORSE HAIR SECTION ON A STRETCHING FRAME (LIGHT BEAM INTO PAPER)

tudinal sections are needed for this work, as even a 4 μ section of solid keratin absorbs about 50% of the incident radiation in the wavelength range 250-290 mμ. These sections were cut with a microtome using razor blades, and their thickness, which was measured by an interference method similar to that reported by Thomson *(4)*, was $\pm 0.3\mu$ of the microtome setting of 4 μ. The section was mounted on a stainless steel stretching frame by cementing the ends with Epikote 834 resin, as shown in Figure 1b. The device was placed inside a 10 mm fused silica cuvette behind a rectangular aperture 0.13 mm wide and about 70 mm high, in such a way that the specimen covered the entire aperture. Generally the cuvette was filled with a suitable immersion medium to reduce surface scatter (see below). A second cuvette, containing immersion medium only, was placed behind a similar slit, and the entire slit assembly mounted on the sliding specimen carriage to allow either specimen or blank to be introduced into the beam for absorbance measurements. Provision for accurate positioning of the slits in the beam was made by external stops.

The choice of immersion medium presented some difficulty as all liquids, such as *o*-dichlorobenzene, which are known to match the refractive index of keratin at the sodium D line, absorb strongly in the interesting wavelength range below about 300 mμ. However, even if a "matching" liquid could be found, which transmitted further into the ultraviolet region, its refractive index is unlikely to be the same as that of keratin throughout the spectrum. This applies particularly in a region of absorption where the dispersion curve exhibits an anomaly. (In any case, surface scatter cannot be eliminated completely, at least with unpolarized light, because keratin is birefringent; the refractive indices (n_D) for light polarized parallel and perpendicular to the fibre axis are about 1.555 and about 1.545 respectively.) Glycerol appears to be the least unsatisfactory immersion medium; its refractive index ($n_D = 1.473$) approaches that of keratin, and it transmits down to about 230 mμ. Moreover, the mismatch between solid keratin and glycerol is not as serious as it would be with a suspension, because a section has only two external scattering surfaces. Many tests, such as the effect of pH or urea on the spectrum of keratin, have to be carried out in aqueous solution. In this case the difference between the refractive index of the immersion medium and that of keratin is considerable and gives rise to a great deal of scattering.

The scattering correction is based on an extrapolation procedure from a non-absorbing region, which in the case of keratin lies at wavelengths above about 400 mμ. In the visible region, therefore, attenuation of the light intensity is due to scattering only and is relatively small if a proper immersion medium is used. Under these conditions, even slight impurities either on or in the specimen, or on the stretching device, give rise to large errors in the scattering correction; it was found necessary to extract the stretching device (with specimen mounted) with Analar petroleum ether (40°-60°C.) for about 30 min in a Soxhlet Extractor and wash it in cold Analar ethanol prior to each test. It was also essential to determine the "cell correction" which corrects for the mismatch in the silica cells, the immersion fluid, and the specimen slits separately for each test. This was done by displacing the specimen in the cell to remove it from the beam, while leaving the rest of the arrangement unaltered and obtaining absorbances at a number of points throughout the spectrum.

Scattering Correction

Unless the results are corrected for scattering of the specimen, little information can be obtained from the experimental spectra. (At the keratin absorption peak in the vicinity of about 280 mμ, about 10% of the attenuation is due to scattering in the case of glycerol, and nearly half the light is lost by scattering if water is used as an immersion medium.) Various attempts to do so have been reported in the literature, but none of these are really satisfactory. For example, Goodwin and Morton *(5)* extrapolate linearly from 340 and 370 mμ into the region of interest, about 270 mμ, and a similar procedure was suggested by Beaven and Holiday *(6)*. This type of method, which assumes a linear variation of scattering with wavelength, is probably valid only when the scattering is small. Keilin and Hartree *(7)* correct the experimental absorption spectrum of a suspension of pigmented particles by obtaining curves with the cuvette at different distances from the detector and extrapolating to zero distance. The authors state that this method is valid only in the wavelength range 500-600 mμ where the scattering is small.

Probably the least unsatisfactory method is that suggested, among others, by Schramm and Dannenberg *(8)*, and later used by various authors, including Schauenstein *(9,10)*, Treiber *(11)*, and Walker *(12)*. It is based on the following considerations; In a region of pure scattering, the absorbance (A) is related to the wavelength (λ) by the expression *(14)*:

$$A = k\lambda^{-x} \qquad [1]$$

where x is an index, which is essentially a function of particle size, and k is a factor which under favorable conditions does not change appreciably with wavelength, λ. In a region of no absorption, therefore, the plot of log A against log λ is a straight line of slope $-x$. When the particle size is less than about $\lambda/20$, i.e., about 150 A for ultraviolet light, x is 4 (Rayleigh scattering). For larger particles, the value of x decreases *(15)* and reaches a value of about 2 when the particle size is of the order of λ.

When absorption occurs as well as scattering, the plot of log A versus log λ deviates from a straight line towards higher absorbances, as A now contains contributions from both scattering and absorption. By extrapolating linearly from the non-absorbing region into the absorbing region and taking the difference between the experimental curve

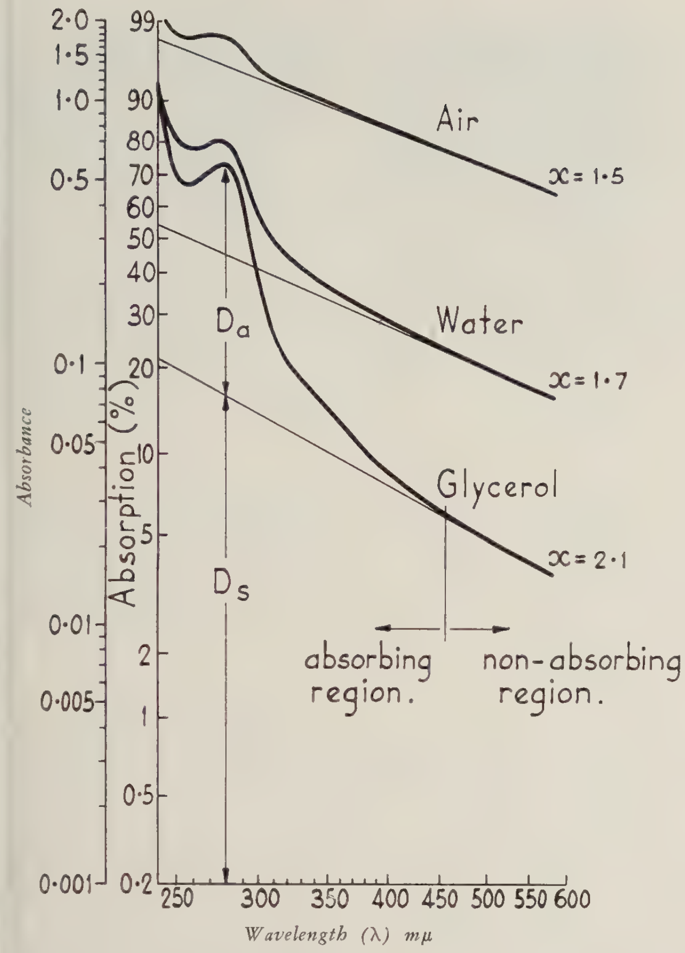

Fig. 2. Ultraviolet Absorption Spectra of a Solid Keratin Section in Different Immersion Media

The true absorbance (D_a) is obtained by subtracting that due to scattering (D_s) from the experimental value. The scattering index x is given by x = tan θ, where θ is the angle between D_s line and abscissa.

and the straight line, the true absorbance (due to absorption only) may be obtained from the graph.

Our correction procedure is substantially that described above, but it is admitted that there are many objections, most of which have been well summarized by Treiber (*11*). Under practical conditions, the technique is essentially empirical, and its justification leans heavily on a number of isolated tests reported in the literature (*8, 10,12*). The errors in the procedure can be greatly minimized by selecting suitable immersion liquids and so reducing the level of scattering.

Results

Typical experimental spectra of keratin are shown in Figure 2, and all show a linear portion, which for air extends to about 400 mμ, while for glycerol it extends to about 450 mμ. The latter curve is undoubtedly more reliable, as small differences in absorbance between the curved and linear portions are masked at high absorbances. At this stage, no explanation can be offered for the difference in values of the scattering index, x. Similar variations have been observed in other tests when the same sample has been immersed in different immersion media.

When the difference between the experimental points and the extrapolated straight line in Figure 2 is plotted against wavelength, the corrected absorption spectrum is obtained (Figure 3). It is seen that the difference between the curves is now quite small. Since the spectrum in air was taken at room humidity, less absorbing material was in the beam than when the sample was in glycerol because glycerol dries the specimen. This effect gives rise to a lower absorbance and is allowed for in the corrected curves.

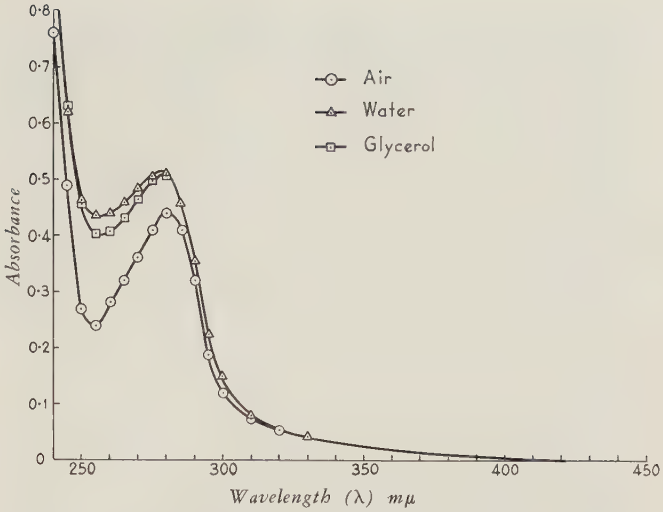

Fig. 3. Corrected Ultraviolet Absorption Spectra of a Solid Keratin Section in Different Immersion Media

Conclusion

The technique described in this report has enabled us to obtain satisfactory spectra of solid keratin. For quantitative work, some caution is required on account of uncertainty in the scattering correction. The technique may be extended to measuring spectra of stretched specimens, spectra with polarized radiation, and difference spectra.

Acknowledgment

The authors thank Dr. E. F. Denby for helpful discussions.

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Submitted May 17, 1960

The Spectrographic Determination of Uranium 235. Part IV. Using a Direct Reading, Littrow, Grating Spectrograph and a Hollow Cathode†

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Abstract

This report, the fourth of a related series dealing with the isotopic analysis of uranium, describes the use of a hollow cathode source and a 4-m, direct-reading, Bausch and Lomb high-resolution spectrograph. A relative precision of ±3.0%, expressed at the 95% confidence level, was obtained with naturally occurring uranium for a single cathode determination of U^{235} measured in twenty min. Evidence for a weak uranium line structure interfering with the U^{235} measurement is presented.

Minor isotopes, U^{234} and U^{236}, present up to a few percent at the higher U^{235} concentrations, did not interfere with U^{235} measurements. Measurements of U^{234}, however, could not be made in the presence of high U^{235} concentrations, thereby limiting the determination of total uranium necessary for calculating the percent U^{235}. At the lower U^{235} concentrations, the concentrations of minor isotopes are generally too small to significantly affect the total uranium content of the sample.

Introduction

This paper‡, the fourth of a related series dealing with the isotopic analysis of uranium, presents an evaluation of a 4-m, direct-reading, Bausch and Lomb high resolution spectrograph, with a hollow cathode source. In the first paper (*1*) of this series, the work of other investigators was cited and the results obtained with dc arc excitation and photographic recording using a Jarrell-Ash Wadsworth spectrograph were described. With the Jarrell-Ash Spectrograph, a direct-reading attachment, and a hollow cathode source described in the second paper (*2*) of the series, a five-fold improvement in the precision was obtained. The third article (*3*), which presented an evaluation using a direct-reading, 22-foot, Eagle spectrograph, indicated a precision comparable with the mass spectrometer from about 30% to 70% U^{235}. The precision was limited, however, by a weak line, which interfered with the U^{235} measurement. This interference was relatively large at the lower concentrations of U^{235}, making precise measurements difficult in the vicinity of naturally occurring uranium (0.712% U^{235}). U^{234} and U^{236} also interfered with the measurement of higher concentrations of U^{235}. To resolve the U^{234} and U^{236} spectral lines from the U^{235} line, and to reduce the effect of the interfering line, particularly at low concentrations of U^{235}, a spectrograph of very high resolving power was needed.

The high resolution Bausch and Lomb spectrograph with direct reading, permitted an examination of the interference and an evaluation of the precision of analysis at the level of naturally occurring uranium.

Equipment

Source and External Optics

The sample was excited in a hollow cathode discharge lamp of the hot cathode type (*2*). The spectral radiation from the source was condensed with a 10 cm lens focussed to produce as nearly a uniform field as possible at the entrance slit. An interference filter was used to minimize background from overlapping orders.

Spectrograph

The 4-m, high-resolution spectrograph (*4*), illustrated in Figure 1, used the 14th order of a plane grating ruled with 309 grooves/mm for a width of 200 mm to provide a reciprocal linear dispersion of 0.23 A/mm. The wavelength drift corrector, consisting of a plane glass plate, allowed compensating for small shifts in the positions of the spectral lines relative to the exit slit. The peak selector mirror allowed positioning the particular isotopic line to be measured over the exit slit and photomultiplier tube.

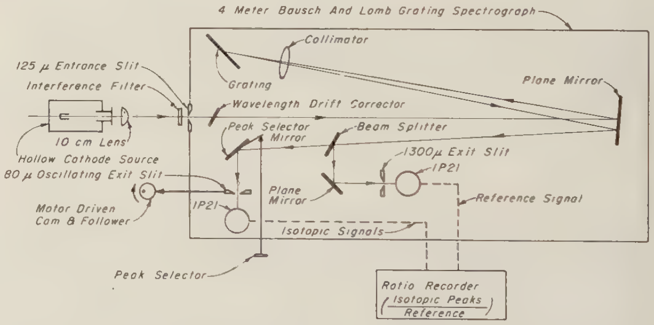

FIG. 1. SKETCH OF EQUIPMENT

Exit Slit Alignment

A peak-scanning measurement technique served to assure alignment of the exit slit with the spectral line. The exit slit and photomultiplier tube were driven back and forth over the spectral line by a motor-driven cam and follower at about 10 cycles/min. The amplitude of the resultant peaks was only a few percent of the height of the total peak. A recording of the output signal was a series of indicating peaks, the tops of which indicated the intensity, while the relative lengths of adjacent bottoms indicated the alignment (see Figures 2A and 2B).

Electronics

The ratios of the signals from the photomultiplier tubes were measured (*5*) as voltage drops across anode load resistors with a ratio recorder. Time constants of

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†This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

*Development Division, Y-12 Plant, Union Carbide Nuclear Company, Oak Ridge, Tenn.

‡The experimental work was completed August 9, 1957 and approved for release on March 3, 1960.

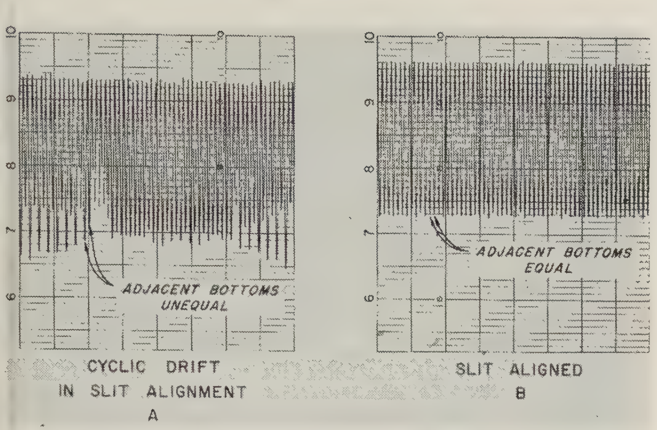


Fig. 2. Indicating Peaks

1 sec for the isotope signal and 5 sec for the reference signal were optimum for the prevailing scanning speeds and rate of source intensity drift relative to the short term signal fluctuations.

Thermal Insulation

A five-min cyclic drift in the alignment between the exit slit and spectral line was indicated by a series of indicating peaks of the U^{238} line recorded over a period of several hrs. The lengths of adjacent bottoms of the indicating peaks alternately became equal and unequal every 2½ min, as shown in Figure 2A. This cyclic drift was correlated with the operation of the room air conditioning system, which cycled within a 2° F control band. The effect was eliminated, as shown by the equal lengths of the indicating peaks in Figure 2B, by insulating the spectrograph housing with aluminum-backed fiber glass.

Vibration Absorbers

The spectrograph was isolated from vibration with layers of cork, felt, and Isomode rubber placed under each leg. The dip in the recording between the U^{234} line and the U^{235} line (Figure 3A) was used as a measure of resolution, since any impairment of the spectral line definition by vibration would raise the dip between these closely spaced lines. No change in the dip was observed with the building air-conditioning equipment (chief source of vibration) turned on and off, indicating that vibration from this source was not impairing the resolution.

Effect of Minor Isotopes

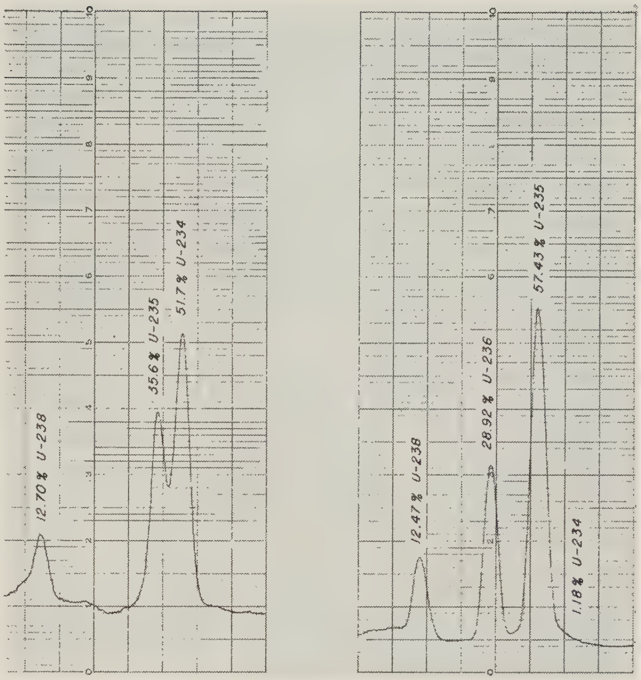
The U^{235} concentration may be expressed as

$$\text{Mole } \% \ U^{235} = 100 \ I_{U^{235}}/I_{U\text{-total}}$$

or, in a system where the concentrations of U^{234} and^{236} are significant, as

$$\text{Mole } \% \ U^{235} = 100 \ I_{U^{235}}/(I_{U^{234}}+I_{U^{235}}+I_{U^{236}}+I_{U^{238}})$$

where I is the photometric intensity, essentially proportional to concentration when properly corrected for background. All of the isotopic lines at 4244 A appear to have identical sensitivities. U^{234} and U^{236}, present up to a few percent at the higher concentrations of U^{235}, are referred to as minor isotopes. The wavelength spacing of the uranium isotopes is shown in Figure 4 (6). Since the concentrations of these isotopes vary independently, it is necessary, if an unbiased determination of the percent U^{235} in the sample be obtained, that the minor isotopes do not interfere with the U^{235} measurement in the numerator, and that the minor isotopes be included in the total uranium measurement in the denominator.



U-234
A

U-236
B

Fig. 3. Resolution of U^{235} from U^{234} and U^{236}

Uranium 235 Measurement

The minor isotopes are adequately resolved on the recordings of Figure 3. Quantitative determination of U^{235} in samples containing as much as 13.5% U^{234}, the closer of the minor isotopes (see Figure 4), agreed well with samples containing no U^{234}.

Total Uranium Measurement

The need for measuring the minor isotopic contribution to the denominator of the equation did not apply at the lower concentrations of U^{235} (below a few percent U^{235}), since at these levels the concentrations of minor isotopes were generally too low to affect the U^{235} analysis.

For accurate determination in samples of high U^{235} concentrations, the problem could be met by measuring each isotope separately and taking the sum, or by measuring a non-isotopic line characteristic of total uranium.

The problem of measuring each isotope separately and taking the sum was examined briefly. A scan of U^{234} and U^{235} indicated insufficient resolution to measure about 1% U^{234} in the presence of 90% U^{235}. Thus the summation of individual isotopic peak measurements was not an acceptable solution when U^{235} was very high in the presence

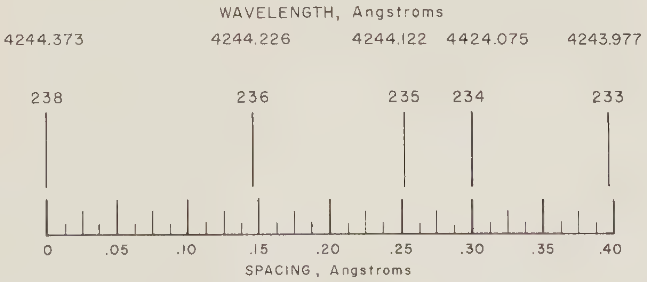


Fig. 4. Isotopic Structure of Uranium Line 4244 A

of very low U^{234} concentration. At more favorable ratios, however, this summation method might be feasible, as indicated by Figure 3A. (The 90% U^{235}, however, was readily measured without interference from the U^{234}, as indicated earlier.)

The second method, measuring a non-isotopic uranium line characteristic of total uranium, was not examined at this time. This method would have required examining several non-isotopic uranium lines and selecting a line showing excitation behavior in the source similar to that of the uranium 4244 line or any other U^{235} line which would have been selected.

Method and Results

Sample Preparation and Excitation

Handling cathodes in groups of 30 or more, approximately 2½ hrs of elapsed time, and about 3 min effort per cathode, were required for sample preparation.

The sample, consisting of 50 mg of U_3O_8, was dissolved in one drop of nitric acid in a glass test tube. The excess acid was driven off by heating, and the remaining uranyl nitrate was dissolved in 1 drop of water. The solution was then transferred to an iron cathode, evaporated to dryness, and ignited to convert the uranyl nitrate to an adhering deposit of U_3O_8. After cooling, the cathode cavity was brushed lightly with a length of pipe cleaner to remove any loose particles, which could cause instability in the discharge.

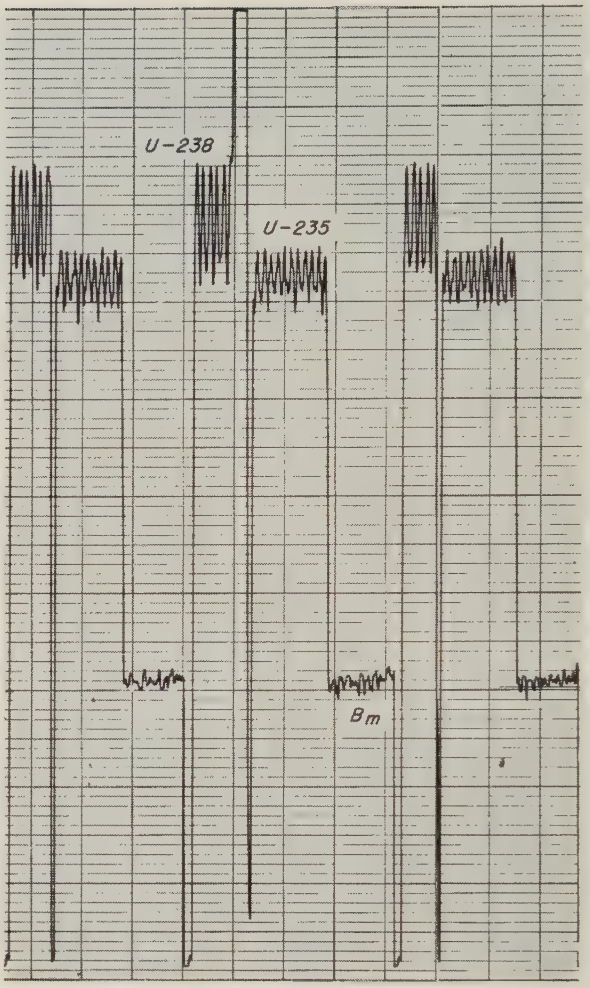
The cathode was screwed onto the high voltage post of the source lamp, and the assembly was screwed into the lamp. The lamp was operated in a continuously flowing atmosphere of argon at a pressure of 6 mm Hg absolute, and excited at 300 ma by a constant current power supply. After 10-15 min pre-burning, the spectral radiation from the lamp reached maximum intensity and measurements were started.

Type of Measurement

Measurements were made of three quantities: U^{235} intensity, U^{238} intensity, and the background intensity. Each intensity was measured on the ratio recorder as a ratio to the reference signal (*7,8*) (see Figures 1 and 5). The three measured intensity ratios, in parenthesis below, were used to calculate the concentration ratio of U^{235} to U^{238}, as follows:

$$\frac{(I_{U^{235}+Bu}/I_{ref}) - k\ (I_{Bm}/I_{ref})}{(I_{U^{238}+Bu}/I_{ref}) - k\ (I_{Bm}/I_{ref})} = \frac{C_{U^{235}}}{C_{U^{238}}},$$

where *Bu* represents the background under each spectral line, which was included in the measurement of the line, *Bm* represents the background measured to one side of the U^{235} line, and *k* is a constant (1.482 at the level of naturally occurring uranium) to make *Bm* equivalent to *Bu*. This constant was calculated from the known concentration ratio and measurements on 20 cathodes containing a standard at the level of naturally occurring uranium and solving for *k* in the above relationship. The constant *k* was not determined for other levels but would be expected to vary with changing concentration of U^{235} because of the complexity of the uranium background. It was assumed in the above expression that *Bm*, adjacent to the U^{235} line, was a suitable background correction for the U^{238} measurement; for the general case where the concentration of U^{238} was much higher than U^{235}, this was satisfactory. The reference signal cancelled out in the above relationship but served to minimize the effect of changes in the source intensity during the 2 min required to measure the intensities of the 2 isotopic lines and the background.



Note: U^{238} measured at 1/50 sensitivity.

FIG. 5. TYPICAL RECORDINGS AT THE 0.712% U^{235} LEVEL

The percent U^{235} was calculated from the concentration ratio of U^{235} to U^{238} as follows:

$$\frac{100\ C_{U^{235}}/C_{U^{238}}}{C_{U^{235}}/C_{U^{238}} + C_{U^{238}}/_{U^{238}}} = 100\ R/(R+1) = \%\ U^{235},$$

where $R = C_{U^{235}}/C_{U^{238}}$.

Precision

The precision was determined at the level of naturally occurring uranium from measurements on 20 cathodes. The average for these cathodes was 0.712% U^{235}. The value for each cathode was the average of 10 repeat measurements made in 20 min. The average precision per set of 10 repeat measurements on the same cathode, representing the internal precision, was ±1.3% of the amount present. The cathode-to-cathode, or sample-to-sample, precision for a single cathode was ±3.0% of the amount present. Both precisions are expressed at the 95% confidence level.

The above precisions for the naturally occurring level were not necessarily those to be expected in typical routine application but may represent the quality of results eventually attainable in routine practice. Among the factors which could influence routine results, several conditions held especially uniform for this evaluation are discussed below:

(1) The uranium oxide samples were obtained in relatively pure form. Prospective routine samples may contain impurities which could affect the uniformity of the cathode deposit and might also contribute variance in spectral background.

(2) The samples were handled as a group, but each of three basic operations, cathode preparation, measurement, and calculation, was conducted by a different operator.

(3) As indicated earlier, the total measurement time for a cathode was 20 min, made up of 10 repeat measurements. Practical routine application would probably require a multiple source assembly (*3*), with attendent multiple optical and electrical components. These additional units would probably introduce sample-to-sample variance involving factors not evaluated in the present study.

Discussion

Although the ±3.0% precision per single cathode would be satisfactory for certain routine applications, improved precision in some cases might be desired. In a previous study (*3*), it was shown that a weak line at approximately 4244.09 A limited the precision by interfering with the U^{235} measurement at 4244.122 A. Further examination of that interference was possible with the higher resolution of the present equipment.

The individual measurements, from which the value for each cathode was obtained, lay in separate families, often without overlap, indicating a distinct factor not statistically random in nature. Experimental evidence that this variance arose from the background was obtained from measurements on 3 cathodes containing a standard with essentially no U^{235} (0.03%). These measurements showed similar cathode-to-cathode variance in the form of families of data. Recordings of these cathodes at the U^{235} position indicated a weak line superimposed on the continuum; the cathode-to-cathode variance introduced by the interfering line could be readily seen.

Recorded scans in the 12, 13, 14, and 15th orders of the standard containing essentially no U^{235} showed the same line structure in each order, and with increasing order number, the intensity of ratio of the structure at the U^{235} position to the U^{238} peak decreased. This indicated that the structure did not arise from an overlapping order and probably was not a grating ghost.

The interference was not associated with either the chemical form of the sample or the cathode material, since 10 iron cathodes and 10 nickel cathodes, each containing 35 mg of uranium metal at about 0.3% U^{235}, showed similar cathode-to-cathode variance in the form of families of data when analyzed for U^{235}. Recordings of an empty iron cathode and an empty nickel cathode, containing no uranium but excited in the usual manner, showed no structure at the U^{235} position. The argon support gas was also free from suspicion, since it was used in the iron and nickel blanks.

Summary and Recommendations

At the level of naturally occurring uranium, a precision of ±3.0% of the amount present, expressed at the 95% confidence level, was obtained for a single-cathode determination measured in twenty minutes. Although adequate for certain routine applications, the precision was evidently limited by a weak interfering line under the U^{235} line at 4244.122 A. Since the interfering line showed excitation behavior different from the U^{238} line, it might be suppressed by changing excitation potential in the source. The problem might be solved by selecting another isotopic line pair, free from interfering line structure.

U^{235} was measured without interference from U^{234} and U^{236}, present up to a few percent. Measurements of the U^{234}, needed to determine total uranium for calculating the % U^{235}, could not be made in the presence of large concentrations of U^{235} because of insufficient resolution. When the concentration of U^{234} is low and not resolvable, the relative error contributed to the U^{235} determination is not appreciably more than the absolute concentration of U^{234}. For refined measurements, a non-isotopic uranium line showing excitation behavior similar to the U^{235} line should be sought for the total uranium measurement.

Acknowledgment

The authors acknowledge the continued encouragement and suggestions of S. Katz during the course of this study. They also extend their appreciation to L. E. Buckhart and J. M. Schreyer of the Y-12 Plant for their cooperation and for the use of the Bausch and Lomb spectrograph.

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Use of Low Molecular Weight Polyethylene in Ultraviolet Spectroscopy*

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Abstract

The ultraviolet spectra of high-molecular-weight materials were obtained by dispersing them in polyethylene, which had a negligible contribution to the spectrum between 2200 and 4000 A. The spectra of reference compounds as well as asphaltenes and polymers are given. The sample is stirred into melted polyethylene, and a portion of the dispersion is pressed between sheets of metal foil in a heated laboratory press to form a film. A circular plate cut from the film and mounted between two metal rings is inserted into the spectrophotometer to obtain a spectrum.

Introduction

The need for a convenient method of obtaining ultraviolet spectra of high-molecular-weight materials, such as asphaltenes (pentane insoluble fractions from crude oils) and polymers (from the naphtha fraction of shale oil), has existed in this laboratory for some time. Solution of complex high-molecular-weight materials is either difficult or impossible in the commonly used solvents such as benzene or the chlorinated hydrocarbons. Frequently the sample is only partly soluble, and the solvent itself has absorption in some part of the ultraviolet region so that a complete sample spectrum is not obtainable.

The potassium bromide technique (*1*) developed for use in infrared spectroscopy has been used in ultraviolet spectroscopy (*1,2*). The production of satisfactory plates is difficult because scattering of the incident radiation by the plates usually produces high background absorption.

Procedure

To prepare a reference plate, 1-3 g of the polyethylene, Epolene C (Tennessee Eastman Co.,), is heated on a laboratory hot plate in a 10 ml beaker (beakers can be cleansed in boiling toluene) until it is free flowing. The polyethylene becomes soft at 80-85° C and tends to flow slowly at 85-95° C. A free flowing material exists at 95-125° C. Above 125° C, fumes are evolved, which indicates decomposition of the polyethylene. Overheating the polyethylene should be avoided in making the melt since a cloudy plate will result.

A portion of the melt is poured onto a sheet of aluminum foil to form a spot about 1.5 cm diam. After cooling, the melt is covered with a sheet of foil, and the sandwich is pressed in a heated (95-100° C.) laboratory press for about one min. The press employed in this laboratory was an hydraulic press having a 1¼-in. ram and 6-in. square, heated plates. The hydraulic pressure employed to press the film was 1000 psi. The temperature to which the laboratory press is heated should be 95-100° C to insure that the polyethylene flows properly and that the resultant film does not adhere to the sheets of metal foil. After one min, the pressure is released, and the sandwich is removed from the press and cooled. The 2 sheets of aluminum foil are then stripped from the film, which has an area of approximately 60 cm. The film is placed between 2 metal rings, 2.5 cm o.d. and 1.4 cm i.d., and a circular plate is cut from the film. The resultant cell is held together with plastic tape on the outside circumference of the rings, and the entire unit is inserted into the instrument to obtain the spectrum.

The same procedure that is used to prepare a reference plate is followed when preparing a sample plate except that the sample is stirred into the molten polyethylene with a mechanical stirrer equipped with a glass stirring rod. Samples having a mp above 100° C are ground and screened to a particle size of —300 mesh before stirring into the polyethylene. Samples that are liquid at 100° C are stirred directly into the molten polyethylene. Weighed quantities of polyethylene and sample are mixed to form the melt. The distribution of the sample in the polyethylene film is an important factor affecting the reproducibility of the intensity of any absorption band. The reproducibility of intensities has been checked in this laboratory by changing the orientation of the films in the instrument. For films that showed even distribution to the eye variations in absorbance of ±0.03 were found.

The sample weight, the total weight of the mixture, and the density of the polyethylene (*3*) are used to calculate the concentration (g/l) of the sample that is present. The thickness (cm) of the final plate is determined by dividing the weight of the final plate by the density of the polyethylene times the area of the plate (cm^2). The density of the mixture is assumed to be the same as polyethylene for these calculations.

Results and Discussion

Polyethylene films that have low absorbance in the 2200-4000 A region can be prepared by the procedure outlined in this paper. The spectrum, obtained on a Cary Model No. 11 double beam spectrophotometer, of a clear polyethylene film is shown in Figure 1, curve 1. Over-

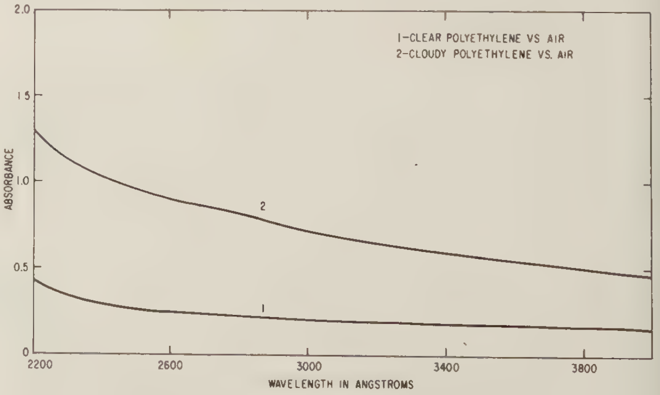

FIG. 1. ABSORPTION SPECTRA OF CLEAR AND CLOUDY POLYETHYLENE FILMS

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*Presented at the 2nd Annual Rocky Mountain Spectroscopy Conference, Society for Applied Spectroscopy, Denver, Colorado, August 1959.

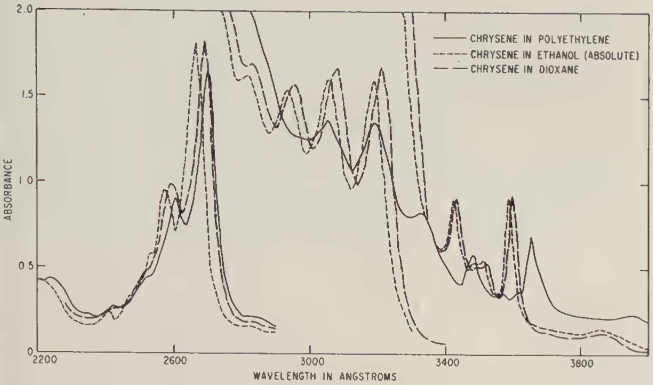

Fig. 2. Absorption Spectra of Chrysene in Polyethylene, Absolute Ethanol, and Dioxane

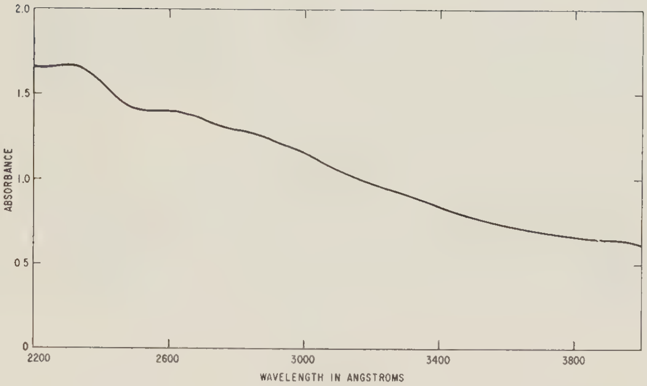

Fig. 4. Spectrum of a Polyethylene Film Containing a Sample of a Pentane-Insoluble Fraction From Petroleum Crude Oil

heating the original melt produces a cloudy plate, and the degree of opacity is directly related to the amount of overheating. The spectrum shown in Figure 1, curve 2, is typical of the increase in absorbance brought about by overheating. The opacity of the film was apparent as a dense cloud in the entire film, and the spectrum of the film in curve 2 shows a relatively high absorbance throughout the entire 2200-4000 A region.

The potassium bromide technique (*1*) of sample preparation has been used in ultraviolet spectroscopy (*2*). Scattering of the incident radiation usually gives background absorbance of approximately 1. A reduction in the amount of grinding gives plates with less scattering but gives uneven distribution of the sample. Plates thinner than 0.058 cm are not rigid and were thus not used. If polyethylene is used for sample dispersion, scattering is not a problem, and the samples can be separately ground and dispersed in the polyethylene by stirring. Little energy is absorbed so that the instrument's resolving power is fully used.

The spectra of samples in polyethylene compare favorably with those in the common solvents used in ultraviolet spectroscopy. This is illustrated for chrysene in Figure 2 and for octahydroanthracene in Figure 3. The spectrum of chrysene is shown in polyethylene, absolute ethanol, and dioxane; the spectrum of octahydroanthracene is shown in polyethylene and absolute ethanol. These compounds were chosen from the many compounds run on the basis of molecular weight and the contrast in fine structure. The well-known solvent effect is apparent in the spectra shown and is much more pronounced for chrysene than for octahydroanthracene. The difference in the amount of shifting of the absorption maxima in the various solvents is to be expected because of the difference in the molecular structures of the compounds. Shifts of the longer wavelength bands are greater than those of the shorter wavelengths band as would be predicted from the solvent effect. A decrease in definition can also be attributed to the same effect. The shifting of the bands does not destroy their relationship to each other within a spectrum. Hence, the ultraviolet spectrum in polyethylene is acceptable for analytical use.

Table I. Molar Extinctions of Chrysene and Octahydroanthracene in Various Media

Compound	*95% Ethanol*[a]	*Polyethylene*	*Absolute Ethanol*
Chrysene	77,620	74,556	72,960
Octahydroanthracene	1,950	2,046	2,372

[a] from (*4*)

The molecular extinctions for the chrysene maximum near 2600 A and for the octahydroanthracene maximum near 2850 A, run in polyethylene and absolute ethanol, were compared to the values obtained in 95% ethanol by Friedel and Orchin (*4*). The values are given in Table I. The values are acceptable considering the purity (approximately 95%) of the compounds and can be used in the usual manner for qualitative analysis.

The spectrum of the pentane insoluble fraction from a petroleum crude oil is given in Figure 4, and the spectrum of some polymeric material formed in shale oil

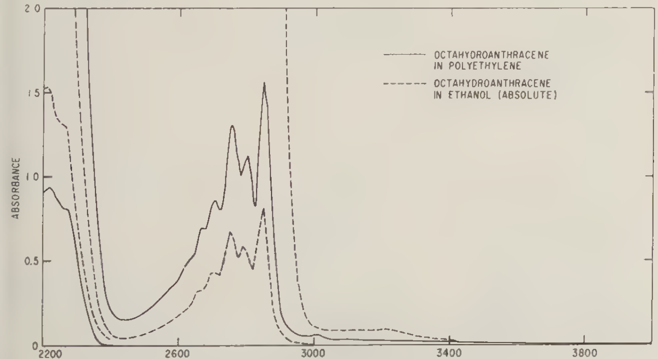

Fig. 3. Absorption Spectra of Octahydroanthracene in Polyethylene and Absolute Ethanol

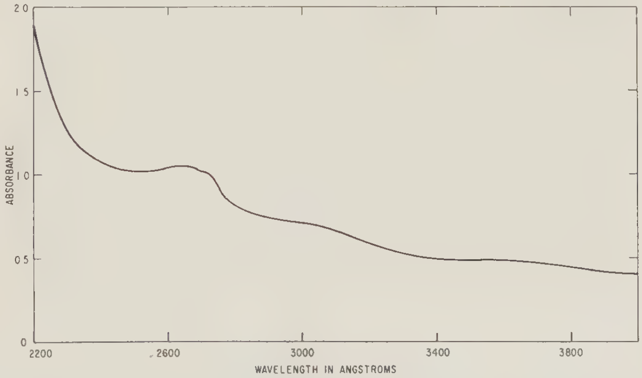

Fig. 5. Spectrum of a Polethylene Film Containing a Sample of a Polymer Formed in a Shale-Oil Naphtha

naphtha is illustrated in Figure 5. The spectra show only broad absorption bands. But the spectra of these same samples in KBr pressed disks showed no bands although the disks appeared to be translucent.

Conclusion

Low molecular-weight polyethylene is useful in ultraviolet spectroscopy as a dispersion medium for samples for which no suitable solvent is available. The thin films of polyethylene, which are recommended, are almost transparent at the most useful ultraviolet wavelengths.

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Infrared Spectra of Aliphatic Normal Mono-Amines and Alpha-Omega Diamines

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Abstract

Solution spectra of aliphatic normal primary mono-amines from ethyl to decyl and of alpha-omega diamines from ethylene to octamethylene are presented, as well as KBr spectra of the diamines. Assignments are made of various bands to structural moieties in the molecule. The solution spectra in each homologous series are markedly similar, but the KBr spectra of the diamines show differences distinct enough for qualitative identification.

Introduction

In the studies being carried out at this Laboratory on the coordination compounds formed between cellulose and amines, the limited information on the infrared spectra of the amino compounds being used became quite evident. Solution spectra of the aliphatic, normal primary amines reported in the literature in the 5000 - 666 cm^{-1} (2 - 15 microns) range are very few in number and so are those of the corresponding aliphatic, alpha-omega diamines. The spectrum for ethylamine in chloroform in this region, reported by O'Connor and coworkers *(9)*, cannot be taken as that of ethylamine since strong evidence for interaction between ethylamine and chloroform is presented by Segal and Jonassen *(13)*. Other reported spectra for methyl- and ethylamines are for the vapors *(2,3,10)*. Spectra for pure butyl- and heptylamines are given only from 2000 - 1000 cm^{-1} (5 - 10 microns) *(1)*. In the near infrared, solution spectra for the series methyl- to amylamine, and also heptylamine, are reported over the range 6802 - 6410 cm^{-1} (1.47 - 1.56 microns) *(6)*, and for octadecylamine from 10,000 - 3571 cm^{-1} (1 - 2.8 microns *(4)*. In the present paper, the solution (CCl_4) spectra of the normal aliphatic amines from ethyl to decyl and of the aliphatic alpha-omega diamines from ethylene to octamethylene are given. KBr spectra are also included for the latter. Assignments of absorption bands to molecular structural units are made, and differences in spectra due to structural differences are pointed out.

Experimental

All of the amine compounds used in this study were obtained as high purity compounds. Except for ethylamine all were further purified by digestion over stick sodium hydroxide, drying with a sodium-lead alloy, and distillation. Cuts were taken when the boiling points reached the literature values. Ethylamine was condensed in glass equipment cooled with ice-water. Samples for infrared examination were sealed in glass ampoules. These were opened in a CO_2-free atmosphere (gloved dry box) in which the CCl_4 solutions and the KBr mixtures were prepared. Specimens of the diamines in KBr were made by adding very small quantities of the diamines to 350 mg portions of pulverized KBr. The specimen discs were then formed from 300 mg of the mixture according to the procedure described by O'Connor and coworkers *(8)*. When the spectrum obtained in this way was too opaque, the quantity used was reduced until a satisfactory spectrum resulted. KBr spectra of the mono-amines could not be obtained because of the volatility of the compounds.

Purity of the amines and the solution concentrations used are shown in Table I.

TABLE I. PURITY AND SOLUTION CONCENTRATIONS OF THE AMINE COMPOUNDS

Compound	*Purity as amine, %* [a]	*Concentration in CCl_4, g/l*
	Normal mono-amines	
Ethyl	100	20.8
Propyl	99	34.7
Butyl	98	25.3
Hexyl	99	30.9
Heptyl	100	22.6
Octyl	99	31.1
Nonyl	98	25.1
Decyl	94	30.6
	Diamines	
Ethylene	98	20.0
Trimethylene	96	37.0
Tetramethylene	99	25.5
Pentamethylene	100	26.4
Hexamethylene	99	18.4
Heptamethylene	99	Insoluble
Octamethylene	95	Saturated

[a] From titration with standard hydrochloric acid with methyl orange indicator for mono-amines and methyl red for diamines.

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†One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Absorption spectra* were obtained using a Perkin-Elmer Model 21** double-beam, recording infrared spectrophotometer with a sodium chloride prism.

Results and Discussion

The spectra of the two groups of compounds will be discussed separately, after which differences and similarities will be pointed out. In the following discussions interpretation of spectra and assignment of bands were made after extensive consultation of several works *(5, 11, 12)*.

The solution spectra of the mono-amines, Figure 1, do not show a large number of absorption bands. There are only slight differences between the spectra regardless of chain length. This is similar to what Liddel and Wulf *(6)* found in the 6802 - 6410 cm^{-1} (1.47 - 1.56 micron) region. Between 5000 and 1111 cm^{-1} (2 and 9 microns) the spectra are almost identical, and only between 1111 and 909 cm^{-1} (9 and 11 microns) lie those bands that may serve to differentiate the compounds.

A rather broad band lying in the region of 4347 - 4000 cm^{-1} (2.3 - 2.5 microns) is apparently an overtone of one of the higher bands since it lies above the functional group absorption frequencies. This could be the second overtone of the band at 1383 cm^{-1} (7.23 microns), a C-H bending vibration. Bands in the 4166 cm^{-1} (2.4 micron) region are also observed in the vapor phase spectra of methyl and ethyl amines listed in Pierson and coworkers' *(10)* catalog of gas spectra, while a 4273 and a 4201 cm^{-1} (2.34 and 2.38 microns) band are found in the solution spectrum of octadecylamine *(4)*. Holdman and Edmondson *(4)* have found that these bands are two of four C-H stretching bands of the $-CH_2-$ group in long chain molecules. The extremely weak band in the 3636 cm^{-1} (2.75 micron) region is also found in the spectrum of octadecylamine (4) as two bands at 3676 and 3636 cm^{-1} (2.72 and 2.75 microns), but no assignment was made.

The weak band at 3413 cm^{-1} (2.93 microns) is an N-H stretching of the $-NH_2$ group. Whether this is a free or bonded $-NH_2$ group cannot be stated conclusively. It lies at the edge of the bonded $-NH_2$ stretching region, but it's location is precisely that expected for a free $-NH_2$ symmetrical stretching mode. According to Jones and Sandorfy *(5)*, primary aliphatic amines exhibit two free $-NH_2$ stretching bands, the symmetrical mode at 3401 cm^{-1} (2.94 microns) and the asymmetrical mode at 3496 cm^{-1} (2.86 microns). Mason *(7)* also lists two $-NH_2$ stretching bands in this region. However, a stretching mode at 3496 cm^{-1} (2.86 microns) fails to show in the spectra presented in Figure 1. The reason for this and the fact that the absorption intensity of the 3401 cm^{-1} (2.94 micron) band is quite weak is not clear at present. In the vapor phase spectrum of ethylamine given by Pierson and coworkers the two bands do appear, but apparently as bonded $-NH_2$ stretchings since the band of medium intensity is located at about 3344 cm^{-1} (2.99 microns) and the weaker band at about 3225 cm^{-1} (3.1 microns).

The strong absorptions at 2941 and 2873 cm^{-1} (3.40 and 3.48 microns) are clearly the asymmetrical and symmetrical C-H stretchings of the $-CH_2-$ groups.

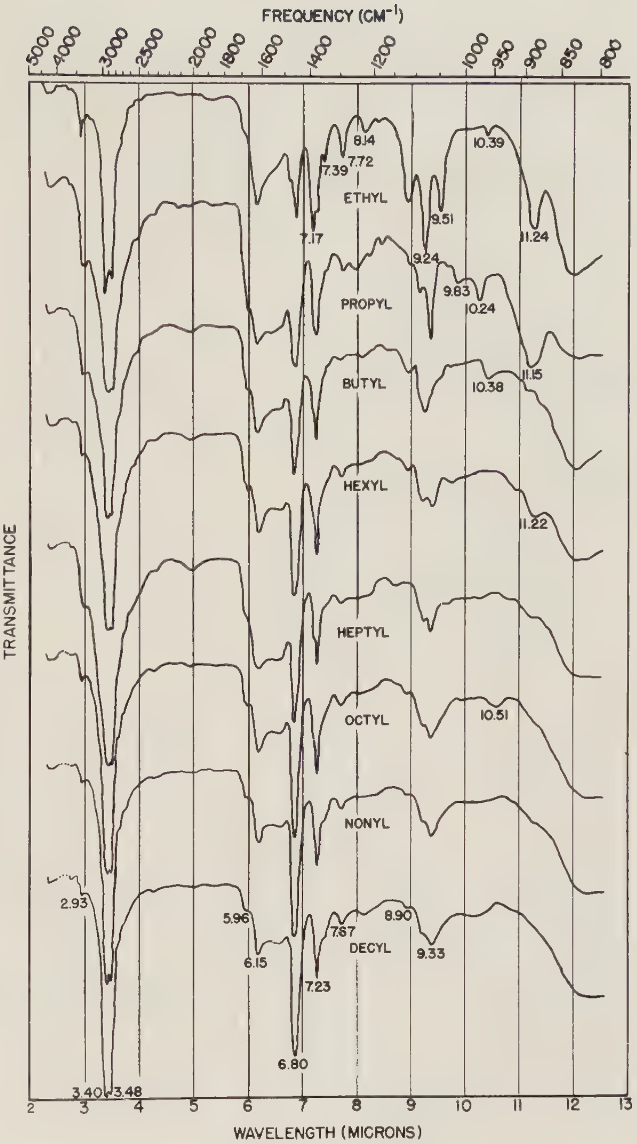

FIG. 1. SOLUTION SPECTRA OF NORMAL MONO-AMINES FROM ETHYL TO DECYL

Another puzzling feature seen in the spectra is the shoulder at 1677 cm^{-1} (5.96 microns). The vapor phase spectrum of ethylamine *(10)* also shows a strong absorption in this region, located at about 1851 cm^{-1} (5.4 microns). Skipping over to 1526 cm^{-1} (6.55 microns) discloses another very weak indication which seems closely related to the 1677 cm^{-1} (5.96 micron) band. The 1526 cm^{-1} (6.55 micron) band indicates a C=O group adjacent to an -NH group, and this, with the 1677 cm^{-1} (5.96 micron) band, suggests the presence of a nonsubstituted amide grouping, except that the 3333 cm^{-1} (3.0 micron) band for such a grouping is lacking. There seems to be no reason for amide bands here and certainly not any amine bands. Randall *et al. (11)*, however, mentions primary amines as one of several known exceptions having bands falling in the double-bond region—these are his "special invariant groups of unknown mode of vibration."

The $-NH_2$ scissoring mode is clearly seen at 1626 cm^{-1} (6.15 microns); the C-H bendings of the chain are located at 1470 and 1383 cm^{-1} (6.80 and 7.23 microns). At 1303 cm^{-1} (7.67 microns) appears the $-CH_2-$ wagging mode. In the C-N and C-C stretching region from 8 microns on out, certain bands can be assigned to C-N

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*All spectra were obtained at a chart speed of 0.5 micron/min, with following program schedule; Resolution at 927, Gain of 6, Response of 1, and Suppression of 3. Cell thickness, NaCl, was 0.48 mm.

**Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

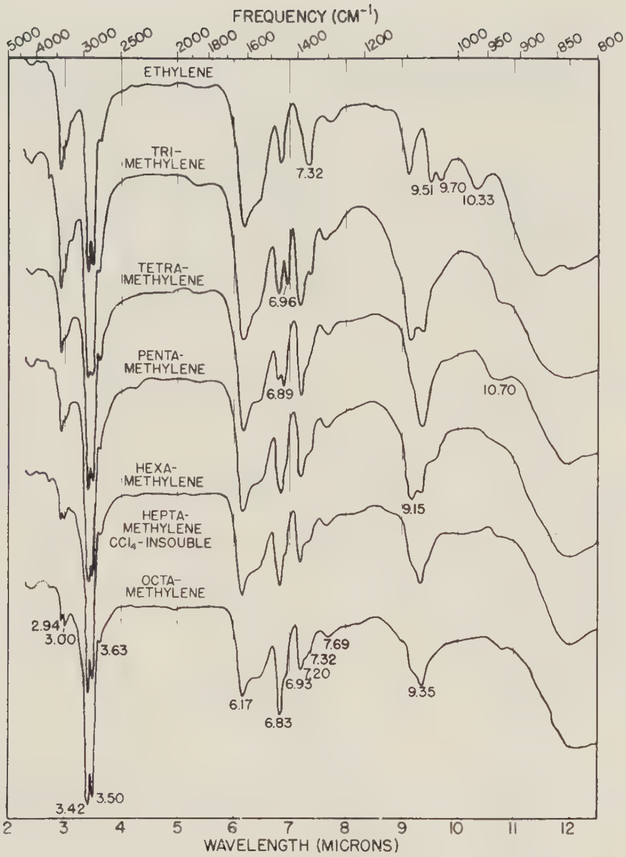

FIG. 2. SOLUTION SPECTRA OF ALIPHATIC ALPHA-OMEGA DIAMINES FROM ETHYLENE TO OCTAMETHYLENE

stretching vibrations. These are the 1123, 1095, and 1071 cm^{-1} (8.90, 9.13, and 9.33 micron) bands. The 892 cm^{-1} (11.2 micron) band which is also present in this region has been reported as an external deformation of the -NH$_2$ group of primary amines (Bellamy *12*). Randall (*11*) reports a C-N stretching at 892 cm^{-1} (11.20 microns) in the Raman spectra of ethylamine.

Although the chain length of the amines increases progressively to ten carbon atoms, no progression indications, as reported by Sinclair and coworkers *(14)* for saturated fatty acids, appear in the amine spectra. One possible explanation for this is that the effect requires a certain minimum number of methylene groups before it will appear.

The solution spectra of the aliphatic alpha-omega diamines, Figure 2, and those of the mono-amines exhibit only a small number of absorption bands. Neither do the spectra show any evidence of effects of increasing chain length, and only in the case of ethylenediamine can the inductive effect of the terminal amine groups be considered as a factor perturbing the molecular vibrations.

In the spectra of the diamines, many of the absorption bands are, as would be expected, quite the same as for the mono-amines. An overtone band appears at 4166 cm^{-1} (2.40 microns) which again may be the second overtone of the C-H bending band at 1388 cm^{-1} (7.20 microns); the weak band at 2754 cm^{-1} (3.63 microns) may be the first overtone. The -NH$_2$ stretching bands of primary amine shown at 3401 and 3333 cm^{-1} (2.94 and 3.00 microns) appear to be bonded. Although the reduction in intensity suggests less bonded -NH$_2$ with increasing chain length, no free -NH$_2$ bands appear. The C-H stretching modes are located at 2924 and 2857 cm^{-1} (3.42 and 3.50 microns), while the -NH$_2$ scissoring mode is at 1620 cm^{-1} (6.17 microns). The bands at 1464 and 1388 cm^{-1} (6.83 and 7.20 microns) are the C-H bendings, while the -CH$_2$-wagging vibration is located at 1300 cm^{-1} (7.69 microns). The -CH$_2$- scissoring vibration could give rise to the 1432 - 1436 cm^{-1} (6.98 - 6.96 micron) band. C-N stretching bands are developed at 1092 and 1069 cm^{-1} (9.15 and 9.35 microns) for most of the diamines, and at 1051, 1030, and 968 cm^{-1} (9.51, 9.70, and 10.33 microns) for ethylenediamine.

The great similarity of the spectra of the mono- and the diamines is illustrated in Figure 3. The spectra of the short-chain, odd-carbon amines and the long-chain, even-carbon amines are markedly similar except in the regions of 3333, 2777, and 1449 cm^{-1} (3.0, 3.6, and 6.9 microns). An explanation of these differences cannot be made from the data at hand. The structures of the amines are related as shown below,

$$\text{H-CH}_2\text{-}(\text{CH}_2)_n\text{-NH}_2$$
$$\text{H}_2\text{N-CH}_2\text{-}(\text{CH}_2)_n\text{-NH}_2$$

where a terminal proton in the mono-amine has been replaced by an -NH$_2$ group, to form the diamine. In the diamine a plane of symmetry exists such that half of the molecule is a mirror image of a primary aliphatic mono-amine,

$$\text{NH}_2\text{-}(\text{CH}_2)_n\text{—}(\text{CH}_2)_n\text{-NH}_2$$

thus one could expect much mono-amine character in the spectra of the diamines.

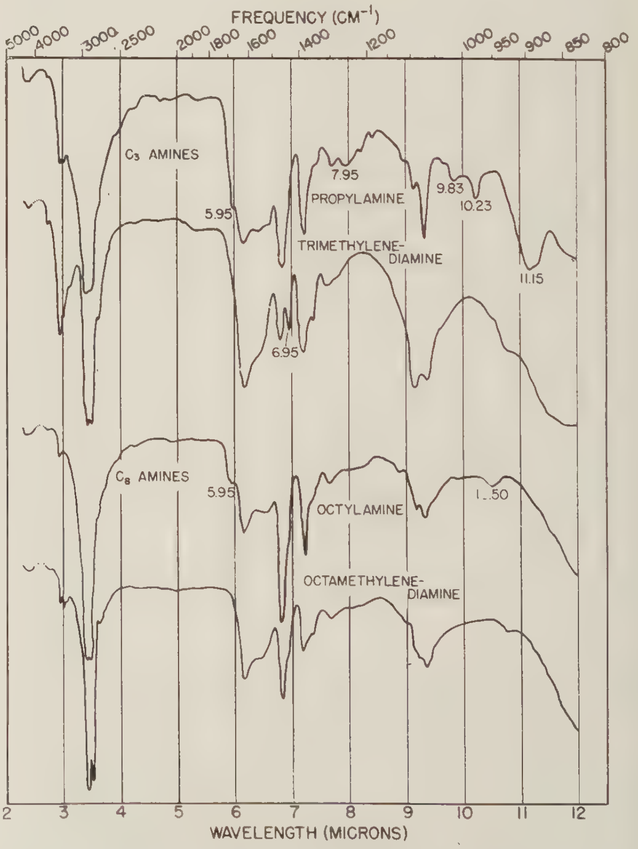

FIG. 3. COMPARISON OF THE SPECTRA OF PROPYLAMINE AND TRIMETHYLENEDIAMINE, AND OF OCTYLAMINE AND OCTAMETHYLENEDIAMINE

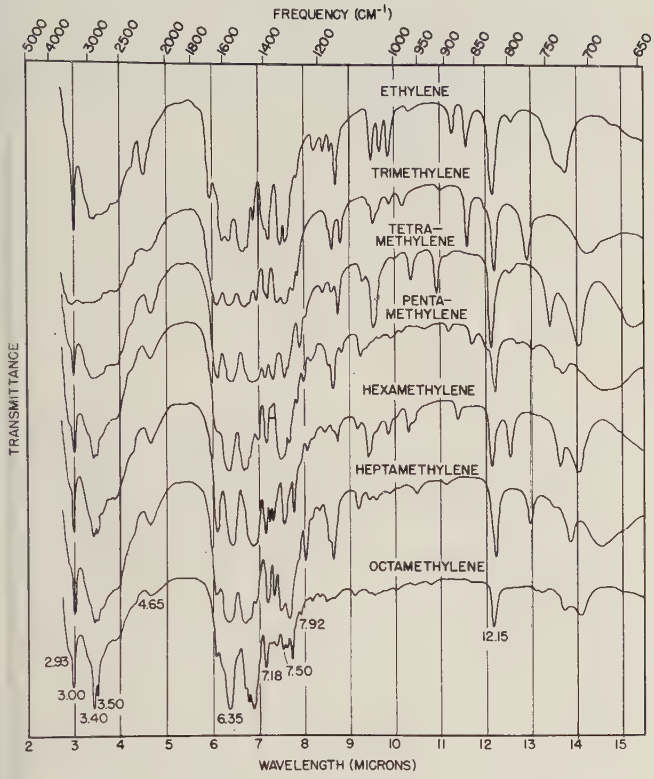

Fig. 4. KBr Spectra of Aliphatic Alpha-Omega Diamines from Ethylene- to Octamethylenediamine

KBr spectra of the diamines, Figure 4, on the other hand, show a multiplicity of absorption bands, and those bands from 1666 cm^{-1} (6 microns) on out are sufficiently different that they can serve for identification purposes. Differences between solution and KBr spectra are more clearly seen in Figure 5. Considering the sample-holding KBr disc as a porous matrix in which the liquid sample is dispersed (where the diamine is not a solid at room temperature) it becomes apparent that the spectrum obtained in this way is in many respects a liquid film spectrum. In that situation, then, as with the solid diamine, many new vibrations as observed in Figures 4 and 5 are to be expected because different combinations of vibrations become possible. Not to be overlooked also are effects arising from interaction between the diamines and KBr. Many combination bands can appear now. Of all the absorption bands observed in the spectra, only ten are common to all of the diamines. Because of the large number of diamines, no attempt will be made to analyze each individual spectrum. Five of the ten bands are vibrations of the primary amine group: three stretching modes in the 3448, 3333, and 2173 cm^{-1} (2.9, 3, and 4.6 microns) regions, the scissoring mode in the 1587-1562 cm^{-1} (6.3 - 6.4 micron) region, and the rocking or twisting mode in the 823 cm^{-1} (12.15 micron) region. The presence of the 2173 cm^{-1} (4.6 micron) band supplies strong evidence that the -NH$_2$ group is highly associated in the undissolved diamine. The band appears in the vapor phase spectrum of ethylamine given in Pierson's catalog *(10)* but has been given only scant attention in other works *(11, 12)*. The indication of high association in the diamines is also evidenced by the high boiling points of the diamines, ranging progressively from 117 to 240°C, as compared to the 16 - 180°C range for the corresponding mono-amines.

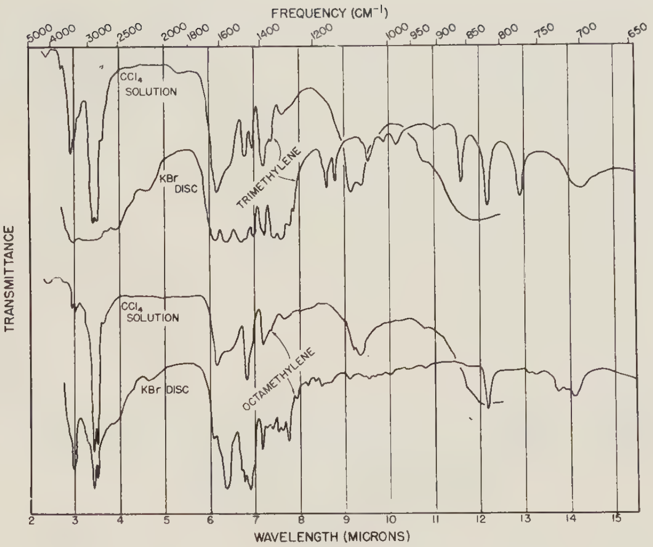

Fig. 5. Comparison of Solution and KBr Spectra of Short and Long Chain Diamines

The band in the region of 1639 cm^{-1} (6.10 microns) is attributed to the presence of water of hydration. The diamines hydrate readily, and it is difficult to keep them absolutely anhydrous.

There are four C-H absorption bands: the C-H stretchings in the 2941 and 2857 cm^{-1} (3.40 and 3.50 micron) regions, the C-H bending in the 1392 cm^{-1} (7.18 micron) region, and the -CH$_2$- wagging in the 1333 - 1262 cm^{-1} (7.50 - 7.92 micron) region.

The remainder of the many bands in the spectra are combination bands formed from various N-H and C-H stretching and bending vibrations. More detailed studies of the diamines seem indicated in order to explain the wide variations observed in wave lengths of the C-N stretching modes above 1000 cm^{-1} (10 microns).

Acknowledgment

The authors are grateful to Misses E. R. McCall and Z. M. Zarins for obtaining the spectra.

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Submitted October 18, 1960

Note

Infrared Spectra of Ethylenediamine and the Dimethylethylenediamines

Leon Segal and F. V. Eggerton

Southern Regional Research Laboratory†, New Orleans, Louisiana

The coordination compound formed between ethylenediamine and cellulose has already been reported (*1,2*), and a study is in progress concerning the manner in which bonding occurs between the hydroxyl groups of the cellulose and the amino groups of the diamine. Two N-substituted diamines, N,N-dimethylethylenediamine (asymmetrical) and N,N′-dimethylethylenediamine (symmetrical), are on hand for use in an attempt to elucidate the bonding and structure of the cellulose-diamine complex. Infrared absorption spectroscopy was considered an invaluable tool for this structure study, complementing x-ray diffractometry, but its use was quickly hampered by lack of suitable infrared absorption data on the diamines. A search of the literature failed to turn up any spectra for the dimethylethylenediamines, either published or cataloged. Only one paper (*3*) was found for ethylenediamine*, but the published spectrum (liquid film) is only over the range 3500-2700 cm^{-1} (2.85-3.70 microns). In the present paper the infrared spectra of ethylenediamine and the two dimethylethylenediamines are given over the range 2-13 microns (5000-770 cm^{-1}), and the absorption bands observed are correlated with molecular structure.

The dimethylethylenediamines were obtained commercially from the Ames Laboratories** and the ethylenediamine from Carbide and Carbon Chemicals Corp.** as high purity liquids, but each was further purified by digestion over sodium hydroxide pellets. The supernatant layer was decanted, dried with a powdered sodium-lead alloy, and distilled. The boiling points of the cuts taken, and their purities as shown by titration with standard hydrochloric acid were: ethylenediamine, 117-117.5°C. (lit. 116.5°C. anhydrous; 118°C. hydrate), 98.0%; unsymmetrical dimethylethylenediamine, 108.5-110.5°C. (lit. 101-104°; 105-108°C.), 92.6%; and symmetrical dimethylethylenediamine, 118.5-119.5°C. (lit. 119°C.), 90.5%. Samples of each cut were sealed in glass ampoules. The carbon tetrachloride solutions of the diamines were prepared in a CO_2- free atmosphere (gloved dry box). The concentrations of the solutions were ethylenediamine, 19.99 g/1 (0.33 M); unsymmetrical dimethylethylenediamine, 23.90 g/1 (0.27 M); and symmetrical dimethylethylenediamine, 26.59 g/1 (0.29 M).

Absorption spectra‡ were obtained using a Perkin-Elmer Model 21** double-beam recording infrared spectrophotometer with a sodium chloride prism.

In the following discussion, interpretation of spectra was made after extensive consultation of several works (*4*). Assignment of bands can only be tentative and incomplete until verified by deuteration and further study.

The structures of the compounds are;

NH_2-CH_2-CH_2-NH_2	ethylenediamine (EDA)
CH_3-NH-CH_2-CH_2-$NHCH_3$	N,N′-dimethylethylenediamine (symmetrical) (sym. DMEDA)
NH_2-CH_2-CH_2-$N(CH_3)_2$	N,N-dimethylethylenediamine (unsymmetrical) (unsym. DMEDA)

and their spectra are given in Figure 1.

Structurally, EDA has two nitrogen atoms in primary amine groups, while in sym. DMEDA they are in secondary amine groups. Unsym. DMEDA has one primary amine nitrogen and one tertiary amine nitrogen. In all three molecules, the 2-carbon chain has a nitrogen atom at each end. The presence of the CH_3- groups in the DMEDA's would be expected to cause changes in the EDA spectrum in those regions where the CH_3- vibrations are most apparent, and the position of these groups in the molecules would be expected to influence their spectra in the regions where carbon-nitrogen and amine vibrations appear. The spectra of the DMEDA's are distinctive enough, however, to permit differentiation between the two compounds.

In the 3-micron region, the two bands at 2.93 and 3.00 microns (3412, 3333 cm^{-1}) in the spectra of EDA and unsym. DMEDA arise from bonded -NH_2 stretching, unsymmetrical and symmetrical, of the primary amine. The tertiary amine group of unsym. DMEDA has no N-H stretching vibration. In the spectrum of this compound the intensity of the primary amine vibration is diminished. In the spectrum of sym. DMEDA, the single mode at 2.99 microns (3344 cm^{-1}) is the single band of secondary amine stretching. All three compounds have strong absorptions in the 3.39-3.59 micron (2950-2785 cm^{-1}) region where CH_3- and CH_2- stretching vibrations appear.

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†One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

*Since this manuscript was submitted A. Sabatini and S. Califano, SPECTROCHIM. ACTA **16**, 677 (1960), have published spectra of ethylenediamine and deuterated ethylenediamine in the vapor, liquid, and solid states.

**It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

‡All spectra were obtained at a rate of 0.5 micron/min, with the Resolution dial set at 927, Gain of 6, Response of 1, and Suppression of 3. Cell thickness (NaCl) was 0.48 mm.

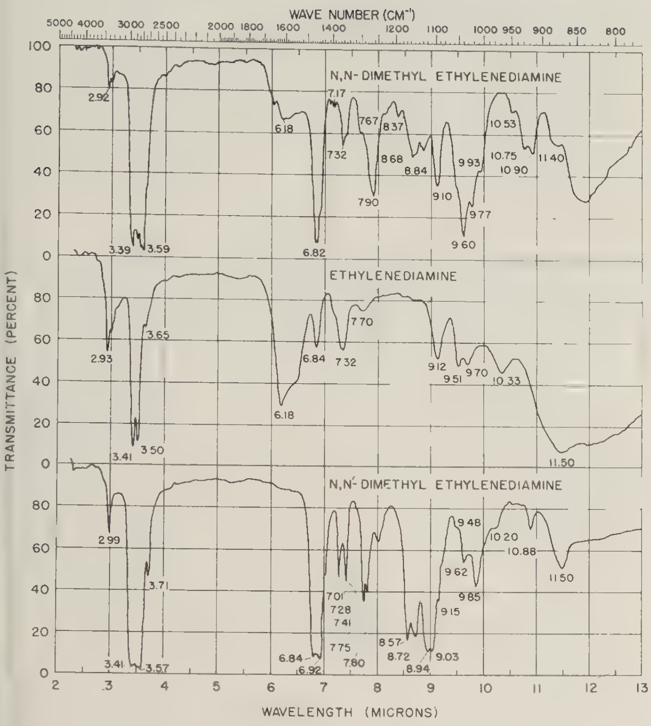

Fig. 1. Infrared Spectra of Ethylenediamine and the Dimethylethylenediamines

The band at 3.55 and 3.57 microns (2817, 2801 cm^{-1}) in the spectra of the DMEDAs is characteristic of the N-CH$_3$ group which is present in these compounds.

The strong band at 6.18 microns (1618 cm^{-1}) for EDA is the -NH$_2$ scissoring vibrations (primary amine). It probably includes some contribution from the H-O-H bending of hydrates because EDA is very hygroscopic, and great pains must be taken to keep the compound absolutely anhydrous. With no primary amine group in sym. DMEDA no -NH$_2$ scissoring vibration would be found, while there is one of moderate intensity at 6.18 microns for unsym. DMEDA.

Also in the EDA spectrum, but lacking for the DMEDA's is a shoulder at 6.5 microns (1540 cm^{-1}), which might be one of the three stretching modes of the N-C-C-N chain. The remaining two modes could be assigned to any of the following: 7.32, 9.12, 9.51, 9.70, or 10.33 microns (1368, 1097, 1050, 1030, or 968 cm^{-1}), but a choice would be difficult.

A marked difference in the spectra is observed at 6.84 microns (1462 cm^{-1}) where the CH$_3$- and -CH$_2$- deformation modes occur. The band in the EDA spectrum is of moderate intensity and arises from -CH$_2$- scissoring only. But for the DMEDAs the contribution of the CH$_3$-bending vibration strongly enhances the intensity of the band. The presence of the doublet suggests an asymmetric bending.

The bands in the 7.28-8.0 micron (1374-1250 cm^{-1}) region arise from C-H bendings, but precise assignments are difficult. The EDA band at 7.32 microns (1366 cm^{-1}) can be assigned to C-H bendings only, as there are no CH$_3$- groups present. The presence of these groups in the DMEDAs, however, is responsible for the rest of the bands in the region.

The CH$_3$- groups exert a noticeable effect on the EDA spectrum in the region from 7.7 to 11.1 microns (1299-901 cm $^{-1}$). The principal C-N stretchings of a primary amine appear in the EDA spectrum at 9.12, 9.51, and 9.70 microns (1096, 1052, 1031 cm^{-1}); the C-N stretchings of secondary amines for sym. DMEDA appear at 8.72, 8.94, 9.03 and 9.15 microns (1147, 1118, 1107, 1093 cm^{-1}). With unsym. DMEDA the absorptions for both primary and tertiary amines appear as would be expected, the primary amine bands being located at 9.10, 9.60, and 9.77 microns (1099, 1042, 1023 cm^{-1}) and the additional tertiary amine bands at 8.13, 8.37, 8.68, and 8.84 microns (1230, 1195, 1152, 1131 cm^{-1}). Now, new bands not in the EDA spectrum, which reflect the perturbation of the C-N stretching of the amine by CH$_3$-groups on the nitrogen atom, appear at 7.90, 8.37, and 9.93 microns (1266, 1195, 1007 cm^{-1}) for unsym. DMEDA, and at 8.02, 8.57, and 9.85 microns (1247, 1167, 1015 cm^{-1}) for sym. DMEDA.

Although it is difficult to assign the bands in the region 10.0-11.5 microns (1000-870 cm^{-1}), the bands at 11.4-11.5 microns (877-870 cm^{-1}) present in all three spectra more probably arise from CH$_2$ and NH$_2$ rocking and wagging vibrations, respectively. The band at 10.75 microns (930 cm^{-1}) in the spectra of unsym. DMEDA seems to arise from the C$_2$-N stretching of the tertiary amine group.

It is clear that only a few of the predicted number of normal fundamental vibrations (30 for EDA and 48 for DMEDA) appear in the spectra. This could be expected because of degeneracies, weakness of intensities, and limited NaCl resolution.

The authors are indebted to Miss Z. M. Zarins for obtaining the spectra.

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Submitted June 28, 1960

* * *

Infrared Quantitative Analytical Data

Publication is open to any person and is not limited to members of the Coblentz Society or the Society for Applied Spectroscopy. Contributions should be sent directly to the Chairman of the Review Committee, Dr. A. Lee Smith, Spectroscopy Laboratory, Dow Corning Corporation, Midland, Michigan. It is requested that methods be submitted in quintuplicate, using the standard format. Infrared spectra cannot be published as a part of this program.

Determination of C_8 Alkylbenzenes (o-Xylene, m-Xylene, p-Xylene, and Ethylbenzene)

J. A. CASTELLANO, Ultra Chemical Works, Inc., Paterson, New Jersey

CS-158

Component			Range %	Accuracy %	λ or ν B.L. Pts.	Slit (mm) Δλ or Δν	Concn. mg/ml Length (mm)
No.	Name	Formula					
1	1,4 Dimethylbenzene	C_8H_{10}	0-25	±0.5	12.6μ 12.3-12.9	0.384 0.049	50 0.0514
2	1,3 Dimethylbenzene	C_8H_{10}	0-60	±0.5	13.0μ 12.8-13.3	0.426 0.055	50 0.0514
3	1,2 Dimethylbenzene	C_8H_{10}	0-30	±1.0	13.5μ 13.1-13.9	0.506 0.065	50 0.0514
4	Ethylbenzene	C_8H_{10}	0-30	±1.0	14.4μ 14.0-14.8	0.750 0.096	50 0.0514

Instrument: Perkin-Elmer Model 137 Infracord, NaCl prism, normal slit program
Sample Phase: Solution in Cyclohexane
Cell Windows: NaCl
Absorbance Measurements: Base Line......X...... Point...........
Calculation: Inverted Matrix......X...... Successive Approx............
Graphical...........

Relative Absorbances—Analytical Matrix:

Component/λ	*12.6μ*	*13.0μ*	*13.5μ*	*14.4μ*
1	0.261	0.006	0.000	0.006
2	0.000	0.250	0.000	0.005
3	0.000	0.002	0.432	0.043
4	0.000	0.008	0.000	0.155

Material Purity: Reference compounds 99+% pure.

Comments: Relative absorbances are given as the slope of the Beer's Law concentration curves used and are expressed in terms of absorbances per 100% of constituent.

Determination of γ-Cyanopropyltrichlorosilane in Methyl (γ-cyanopropyl) dichlorosilane

PHILIP J. LAUNER and ALFRED S. CROUSE, Silicone Products Department, General Electric Company, Waterford, New York

CS-159

Component			Range %	Accuracy %	λ or ν B.L. Pts.	Slit (mm) Δλ or Δν	Concn. Vol. % Length (mm)
No.	Name	Formula					
1	γ-Cyanopropyltrichlorosilane	$C_4H_6Cl_3NSi$	0-2	±0.1	16.78μ	0.900	16.7[a] 0.970

Instrument: Perkin-Elmer Model 321, CsBr Prism
Sample Phase: Solution in Carbon Disulfide
Cell Windows: KBr
Absorbance Measurement: Base line........... Point..... X
Calculation: Inverse Matrix........... Successive Approx........
Graphical ... X

Relative Absorbance—Analytical Matrix:

Component/λ	*16.78μ*
1	34.0

Material Purity: 99.8%

Comments: These compounds hydrolyze readily in moist air to give hydrogen chloride and high-molecular-weight siloxanes. For special precautions, which should be taken in handling samples, see Anal. Chem. **31**, 1175 (1959) and APPLIED SPECTROSCOPY **14**, 86 (1960). The I_0 measurement is made using a carbon disulfide solution of pure methyl(γ-cyanopropyl)dichlorosilane in each of two matched cells. For the I measurement, the reference cell is left in the reference beam, and the sample cell is filled with a carbon disulfide solution of the unknown. Relative absorbance is given as the slope of the Beer's law concentration curve used and is expressed in terms of absorbance per 100% of constituent.

[a] One ml of sample is added to five ml of CS_2.

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Society News

Governing Board Meeting

The Governing Board of the Society for Applied Spectroscopy met in the Hilton Hotel in Chicago on May 17, 1961. Mr. Neil Gordon presided. Dr. Marvin Margoshes reporting for the Journal Award Committee announced that the committee had nominated four papers from among those published in Volume 14 of Applied Spectroscopy for the award. The committee voted the award to "The Spectrochemical Analysis of Solutions. A comparison of Five Techniques" by William K. Baer and Edwin S. Hodge. It is planned to present the award of $100 donated by Arthur Mittledorf at the Eastern Analytical Symposium in November.

Mr. Zink presented a report from Dr. Frederick Strong, III, Editor-in-Chief of Applied Spectroscopy, which took issue with the present operation of the journal. After considerable discussion, the Governing Board resolved that the Executive Committee appoint a committee to investigate the operation of the journal and report by September 1st.

Mr. Zink reported that the S.A.S. Bibliotheca Central de Spectroscopia had published four issues, which printed the titles of some 600 papers in spectroscopy.

A resolution was passed that anyone wishing to speak publicly on any project or business that pertains to the Society first request authorization from the Executive Committee.

The Conference Committee proposed several recommendations. The report defined a local meeting as any meeting sponsored by one Local Section; a regional meeting as any meeting sponsored by one or more Local Sections; and a national meeting as any meeting sponsored by the National Society. The Committee encouraged the promotion of Local and Regional Meetings whenever possible. It recommended that the Society sponsor one national meeting a year to be held in September, October, or November; that this national meeting be rotated among the various regions by petitions from the Local Sections; and that exhibitors be requested to exhibit only at the national meeting unless exhibitors should desire to show at a local meeting. Petitions for the 1963 meeting should be in the hands of the Executive Committee by October 1, 1961.

Nominations

The Nominating Committee presents the following list of nominees:

President-Elect

Dr. Donald R. Johnson, Research Supervisor, Supporting Chemistry and Analytical Chemistry, Polychemicals Department, Research and Development Division, E. I. du Pont de Nemours, Wilmington, Delaware.

Dr. Claude A. Lucchesi, Supervisor, Analytical Research and Services, Mobil Chemical Co., Paulsboro Laboratory, Paulsboro, N. J.

Dr. Johnson received a B. A. from the University of Minnesota and a Ph. D. from the University of Wisconsin in 1954. He has been employed at du Pont since graduation. As Research Supervisor, his interest extends to all branches of spectroscopy — infrared, Raman, N.M.R., emission, x-ray and mass.

He was chairman of the Delaware Valley Section of S.A.S. in 1960, and this year is a delegate from his section.

Dr. Lucchesi received his B. S. from the University of Illinois in 1950 and his Ph. D. from Northwestern University in 1954. Upon graduation, he joined Shell Development Co. as a research chemist, becoming Group Leader in Spectroscopy. From 1956 until this summer when he accepted his present position, he was Director of the Analytical Research Department of Sherwin-Williams Co.

He has been active in the Chicago Section of S.A.S., being vice-chairman in 1959 and chairman in 1960. He has also served as a delegate from this Section. His chief fields of spectroscopic interest are infrared and x-ray.

Secretary

Reverend J. J. Devlin, S. J., Department of Physics, Boston College, Boston, Mass.

After discussion with several members of the Executive Council, the Nominating Commitee has decided that it is in the best interests of the Society that the office of Secretary be kept for the present, at least, at Boston College. They have accordingly asked Father Devlin to allow his name to be placed in nomination for another term as Secretary, without opposition, and he has accepted.

The Nominating Committee recognizes the tremendous amount of work that Father Devlin has done for the Society over the past three years, and is grateful that he is willing to continue in his present capacity.

Treasurer

Dr. Isabel H. Tipton, Associate Professor, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee.

Mr. Andrew F. Rekus, Research Chemist, Baltimore Gas and Electric Co., Research Department, Baltimore, Maryland.

Dr. Tipton received her B.S. from the University of Georgia and her Ph. D. from Duke University. After ten years as a wife and mother of four children, Dr. Tipton joined the staff of the University of Tennessee in 1948. Since that time, she has risen from the rank of instructor through assistant professor to her present position as associate professor. In addition to her teaching duties, she is director of the program of spectrographic analysis of human tissue, under the Health Physics Branch of Oak Ridge National Laboratory.

Dr. Tipton was chairman of the Southeastern Section and delegate to the Governing Board of S.A.S. in 1959 and 1960. She is currently serving on the Conference Committee of S.A.S.

Mr. Rekus is a graduate of Loyola College, having received his B.S. there in 1941. He has also taken postgraduate work at Johns Hopkins University in emission spectroscopy, flame photometry, petrography, and x-ray diffraction. He was a delegate to S.A.S. from the Baltimore-Washington Section from 1958 through 1961 and has taken an active part on committees of the National Society. He has also been chairman of the Baltimore-Washington Section for 1960-61, and is presently secretary of the Eastern Analytical Symposium.

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Letter

[The Editor will publish as the occasion arises, letters concerned with issues of interest to Spectroscopists]

Meetings

Sir:

As Spectroscopists, we all like to attend conferences and gain valuable information from the papers presented, from the exhibits, and from the "gab fests" with our friends. In 1961, ten conferences will be held which are sponsored by one or more local sections of SAS. This does not include the specialized fields such as the infrared, Raman, mass, x-ray, etc.

Let's stop and review this situation: (1) the organization of such meetings takes a lot of time and effort; (2) such conferences are expensive to operate; (3) there must be a large attendance to be successful; (4) the papers presented must contain useful, informative information; and (5) the instrument manufacturers must have representatives at all conferences and exhibits at most of them. Considering all these points the holding of conferences represents a lot of money and time, so we must insure that our companies are getting value for the money they spend.

Until now, SAS has not taken any position on the conferences held but at the request of one local section, a conference committee was appointed to make recommendations to the Governing Board on the policies concerning the forthcoming conferences. The following recommendations were presented and approved by the Governing Board in Chicago in May 1961.

1. Type of Meetings
   - A. Local—sponsored by one local section.
   - B. Regional—sponsored by two or more local sections.
   - C. National—sponsored by the national society.
2. Recommendations of Meetings
   - A. That Regional meetings be held, if at all possible, as these meettings enable more people to attend a higher calibre meting.
   - B. That SAS sponsor one meeting a year to be held in September, October or November. (Pittsburgh Conference is a local meeting.)
   - C. That national meetings be rotated among the regions by petitions from those groups.

D. That the exhibitors be requested to exhibit only at the national meeting. (They may exhibit at other meetings at their own prerogative.)

3. Form for Petitioning

A. A triplicate written form must be made to the Conference Committee which shall submit it to the Executive Committee then to the Governing Board. The petition must contain: (a) An outline of the tentative organization; (b) The names of the local section sponsoring the meeting; (c) The experience of the group in conducting large meetings; (d) The financial status of the groups; (e) The available space for housing and exhibits; and (f) The approximate number of non-voluntary workers that would be required.

B. The petitions for the 1963 meeting must be submitted by October 1, 1961 so that the final decision of place can be made at the New York Governing Board meeting.

C. The petitions for 1964 and 1965 should be submitted by January 1, 1962.

D. Petitions for the annual meeting must be made a minimum of two years in advance of the contemplated meeting.

4. Conference Committee

A. In order to have continuity, the members of this committee will serve three years.

B. The members of the present committee have been staggered by presidential appointment—three to serve three years, two to serve two years and two to serve one year.

C. All geographical regions will be represented on this committee.

5. Duties of the Conference Comittee

A. Help to organize the national SAS meeting.

B. Aid the regional meetings by helping to promote and strengthen them.

C. Arrange for keynote speakers at regional meetings (if needed) and help finance the cost of providing these speakers if the regional sections is not financially able to pay the speaker.

D. Be the clearing house for all conference details.

E. Give any assistance requested by local or regional sections.

The committee knows that this is just the beginning and that there are many problems that will have to be resolved in the near future. We do feel that the policy concerning the national meeting has been established. It is not within our jurisdiction to tell *any* group that they cannot hold a meeting, as many practicing spectroscopists are permitted to attend regional meetings who never could attend a meeting of national scope unless it was in their region. However, we would like for each group to raise the standard of their meeting by having informative papers that are well presented.

Let us never forget that we, as practicing spectroscopists, must uphold the objectives of SAS in that we must advance and disseminate the knowledge and information concerning the art and science of spectroscopy, etc.

(Continued on page 13A)

S.A.S. Local Section News

Editor—Carl J. Leistner

[Items for this column should be sent to the Editor, Mr. Carl J. Leistner, United Carbon Products Company, P. O. Box 747, Bay City, Michigan.]

Eastern Analytical Symposium

Hotel Statler Hilton, N. Y. November 15-17, 1961

Preliminary Program

Wednesday—A.M.
Detectors for Gas Chromatography, X-ray Spectroscopy, Storage and Retrieval of Infrared Spectral Data

Wednesday—P.M.
Gas Chromatography with High Molecular Weight Polar Organic Compounds, Nuclear Magnetic Resonance, Emission Spectrography

Thursday—A.M.
Mass Spectroscopy, Advances in Physical and Chemical Separations, Automation in Microchemical Analysis

Thursday—P.M.
Advances in Chemical Analysis, Advances in Physical and Chemical Separations, Molecular Weight Methods

Friday—A.M.
Food Additive Analysis, Applications of Radio Isotopes, Electroanalytical Methods

Friday—P.M.
Applications of Nuclear Activation, Electroanalytical Methods

Baltimore-Washington Section

Date: October 3, 1961
Time: 8:00 P.M.
Place: W. R. Grace & Company, Clarksville, Maryland
Program: Group Discussions

Symposium on Research Methods and Instrumentation

Bethesda, Maryland October 10-13, 1961

This Symposium is co-sponsored with the Washington Sections of the American Association of Clinical Chemists, American Chemical Society, Instrument Society of America, Society of American Bacteriologists, and Society of Experimental Biology and Medicine. Examples of the latest types of research equipment will be exhibited by instrument manufacturers.

Monday—8:00 P.M.

Applied Gas Chromatography

Recent Advances in the Analysis of Lipids by Gas Chromatography—S. R. Lipsky

Gas Chromatographic Separations of Steroids and Related Compounds—E. C. Horning, E. O. A. Haahti, and W. J. A. Vandenheuvel

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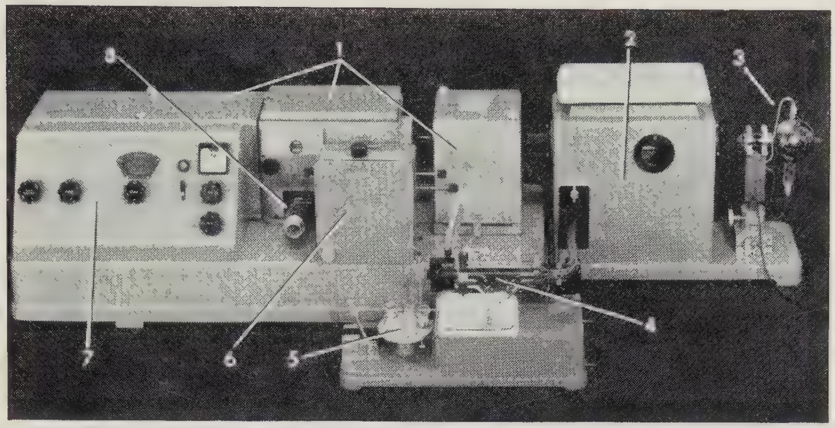

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Application of Gas Chromatography to Amino Acids—D. E. Johnson, Sara J. Scott, and A. Meister

Tuesday—2:00 P.M.

Factors Influencing Interpretation of Spectra

Factors of Importance in the Interpretation of Infrared Spectra—R. C. Lord

Interpretation of Molecular Electronic Spectra—M. Kasha

Factors Influencing the Interpretation of Nuclear Magnetic Resonance Spectra—E. R. Becker

Tuesday—8:00 P.M.

Optical Rotatory Dispersion

The Application of Optical Rotatory Dispersion in Structural Studies of Polyeptides and Proteins—G. D. Fasman

Applications of Optical Rotatory Dispersion to Structural Organic Chemistry—K. Mislow

Optical Rotatory Dispersion Theory and Experiment—E. Charney

Wednesday—2:00 P.M.

Thermogravimetric Analysis

Thermoanalysis: Thermogravimetry and Differential Thermal Analysis—S. Gordon

Recent Thermoanalytical Techniques—P. D. Garn

The Use of Thermoanalytical Procedure in Radiation Effects and Kinetic Studies—E. S. Freeman

Wednesday—8:00 P.M.

Electron Probe Analysis

The Electron Probe Microanalyzer—L. S. Birks

Applications of the Electron Probe Microanalyzer—C. M. Schwartz

Biological Specimen Examination with the Electron Probe X-ray Microanalyzer—E. J. Brooks, A. J. Tousimis, and L. S. Birks

Element Analysis (Cu, Ag, Fe) at the Subcellular Level in Tissue Sections of Human Specimens by Means of the Electronmicroprobe—A. J. Tousimis and I. Adler

Thursday—2:00 P.M.

Application of Physiological Instrumentation to Clinical Problems

Clinical Measurements of Biological Vibrations in Normal and Disease States—M. L. Petrovick and Jo Brumlik

Acquisition of Physiological Data at the Bedside—L. A. Geddes, W. A. Spencer, H. E. Hoff, D. M. Hickman, A. G. Moore, M. Hinds, and M. Guadiano

The Use of Ultrasonic Echo-Ranging to Record the Motion of Heart Walls and Septa—J. M. Reid

(Continued on page 15A)

NO. **75** NMR AT WORK SERIES

HOW NMR SPECTROSCOPY DETERMINES MOLECULAR STRUCTURE

(NUCLEAR MAGNETIC RESONANCE)

Because it uses a unique molecular parameter, NMR Spectroscopy frequently provides a way around the particular ambiguities which block final solution by other spectroscopic or chemical means. NMR gives the clearest indication of the position of hydrogen atoms in the molecule — often the surest key to organic structure determination. And NMR Spectroscopy is fast and non-destructive.

EXAMPLE

NMR spectra of nucleosides

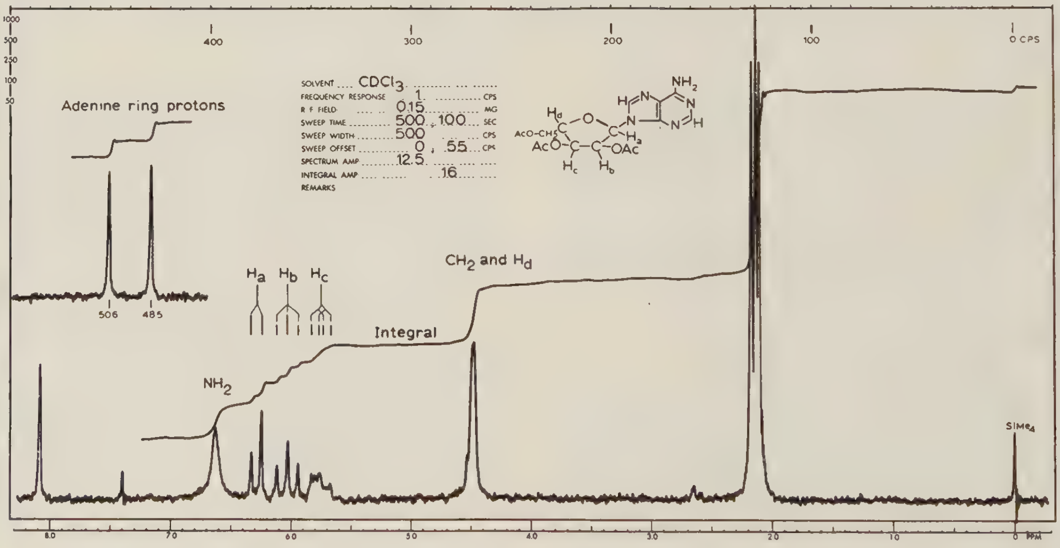
Interpretation: Adenosine, or adenine riboside, forms a triacetate[1] which is soluble in $CDCl_3$. The NMR spectrum of this solution permits assignment of the peaks and correlation with the molecular structure. Chemical shifts are measured in parts per million (δ units) with shifts toward lower field being considered in a positive sense relative to the internal reference material, tetramethylsilane, equal to zero.

The adenine ring protons fall at $\delta = 8.43$ (506 cps.) and 8.09 (485 cps.). These large shifts are characteristic of aromatic protons, particularly heterocyclic rings involving nitrogen. The NH_2 group appears at $\delta = 6.62$ and displays a typical broadening. H_a is spin-coupled to one neighbor, H_b, and is found as a simple doublet centered at $\delta = 6.29$, due to the combined effect of adjacent oxygen and nitrogen which results in the largest shift of any of the ribose protons. H_b is equally coupled to H_a and H_c, resulting in a symmetrical triplet centered at $\delta = 6.03$. H_c is coupled more weakly to H_d than to H_b and the situation is further complicated by the accidental degeneracy of H_d and the CH_2 group which results in an unresolvable complex of lines for H_c. The integral curve confirms the assignments, particularly the overlapping of H_d and the CH_2 group, since the area of the peak at $\delta = 4.47$ is found to correspond to 3 protons.

In accord with these results, the work of Cohn[2] shows that NMR spectra can be of considerable value in elucidating the structures of unusual nucleosides.

(1) Sample supplied through the kind cooperation of Dr. John S. Webb, Lederle Laboratories.

(2) Cohn, W. E., J. Biol. Chem., 235, 1488 (1960).



SOLVENT .... $CDCl_3$
FREQUENCY RESPONSE 1 .... CPS
R F FIELD ...... 0.15 .... MG
SWEEP TIME .... 500, 100 ... SEC
SWEEP WIDTH .... 500 ...... CPS
SWEEP OFFSET .... 0, .55 ... CPS
SPECTRUM AMP .... 12.5 ....
INTEGRAL AMP .... .16 ....
REMARKS

For other examples in this series and for current technical information on Varian NMR and EPR Spectrometers, write the Varian Associates Instrument Division.

VARIAN associates
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(Continued from page 120)

The first SAS sponsored conference will be the International Conference to be held at the University of Maryland, College Park, Maryland, June 25-29, 1962. Let's start making plans now to attend this conference which is less than a year away. *Spectroscopists, this is your conference so make it a success!*

Any suggestions or criticisms of these recommendations should be sent to Mrs. Sarah H. Degenkolb, Conference Committee Chairman, American Steel and Wire Division, Research Laboratory, Wire Avenue, Cleveland 5, Ohio.

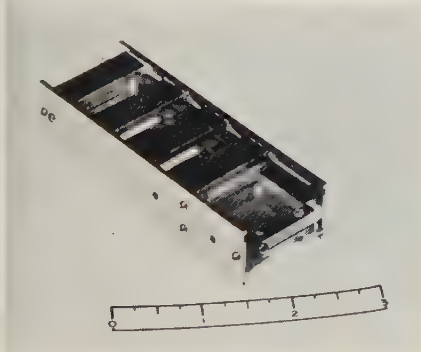
Sarah H. Degenkolb

What's New?—

(Continued from page 7A)

A new special purpose *photomultiplier* has been developed by the Bendix Corporation, Cincinnati Division.

This device covers the spectral range from below 2 to 1500A by the use of a windowless design. It withstands indefinite exposure to moist air and has survived rocket launching for solar spectrum studies. The rise time is less than 5 x 10^{-9} sec and the dark current is less than 0.1 electron/sec referred to cathode.



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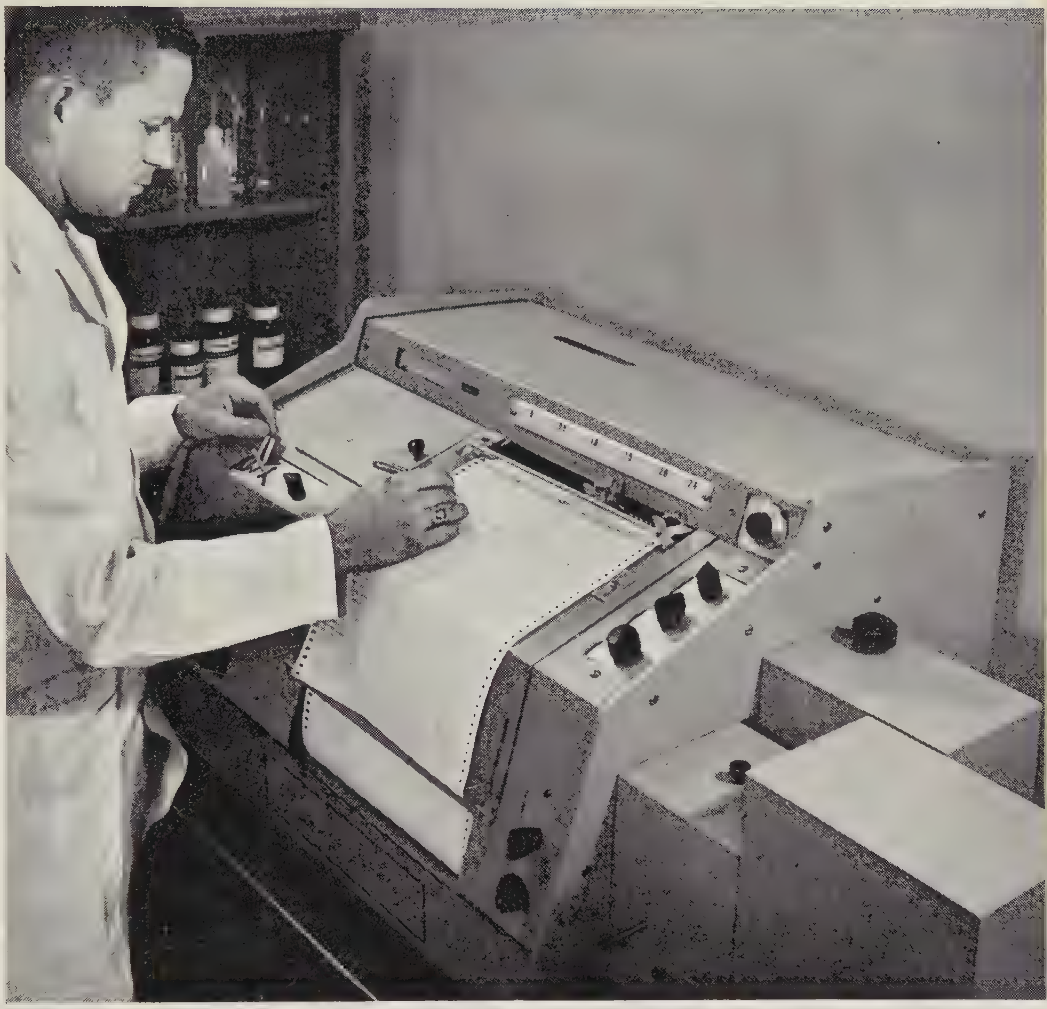
Jarrell-Ash Company, Newtonville, Massachusetts is offering an instrument for *atomic absorption spectroscopy*.

The apparatus consists of a hollow cathode discharge tube, several burners, and a multiple pass attachment all mounted on the optical bar of a high resolution grating spectrometer. The signal is picked up by a photomultiplier and recorded by a high sensitivity recording system.

Cary Recording 15 Spectrophotometer
NEW MODEL



Another fine instrument in the Cary tradition of highest quality is the new Model 15 Recording Spectrophotometer. Significant design advancements contribute to its outstanding, versatile performance. Instrument operating limits, 1750-8000 A, extend precision usefulness over a broader range. Reduced beam size (1.0 x 0.3 cm) assures maximum reliability with minimum samples. Coupled scan and chart drive affords extreme operating simplicity with single variable speed control. For complete technical information on the Model 15, ask for Data File D28-81.

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For preparing KBr pellets use stainless steel or agate vials. Invaluable in the fields of X-Ray Diffraction, Emission Spectrographic Analysis, X-Ray Spectroscopy, Infra-Red Spectroscopy, Metallurgy, Geology, Oil Research, Aluminum Manufacture, Chemical, Paint and Color Analysis, Ceramics, Foods, Agriculture.

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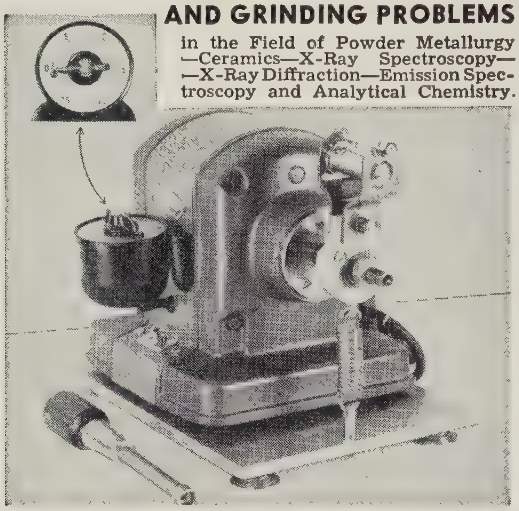

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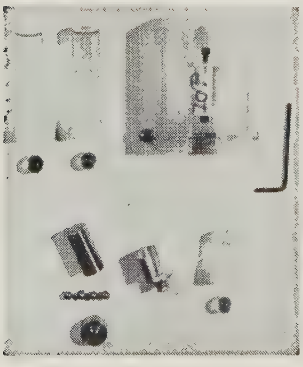
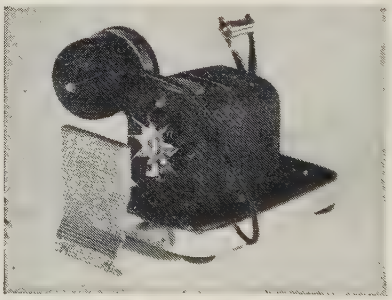
Stainless Steel Vials 6 ml or 10 ml and Rod Pestles or Ball Pestles. Tungsten Carbide 6 ml and 25 ml Vials and Rod or Ball Pestle.



ACCESSORIES FOR 5A OR 3A WIG-L-BUGS

3113 Adapter, for ½" dia. x 1" long vials.
3111 Vial, ½" x 1" polystyrene with cap.
3112 Ball-pestle, clear plexiglas, ⅜" dia.
3115 Adapter for ½" dia. x 2" long vials.
3116 Vial, ½" x 2" polystyrene with cap.
3113 Adapter for ½" dia. x 1" long vials.
3114 Vial, stainless steel ½" x 1" with ball-pestle ¼" dia.
3117 Vial, tool steel (hardened) ½" x 1" with steel ball-pestle ¼" dia.
3118 Vial, agate 9/16" dia. x 1 5/16" long 2 ml capacity with agate ball-pestle ¼" dia. (Requires 3115 adapter).

5A—Wonder Electric Mortar—the action is reciprocating in the form of a figure 8 swung through a 6 ½° arc at 3200 RPM, the ball pestle then strikes the end of the vial some 2000 times in ten seconds. Can be run continuously for 5 minutes (and this depends on the load) with a rest period between the 5 minutes to cool the motor completely.



3A—Model with Fan and 1 hour timer—same type of motor and action as 5A Model but this 3A can be run for 20-30 minutes with cooling off periods between to cool the motor.

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(Continued from page 11A)

The Instantaneous and Continuous Computation of Aortic Blood Velocity from the Spatial Pressure Gradient in Man—S. M. Fox, III, D. L. Fry, A. J. Mallos, J. C. Greenfield, J. R. Warbasse, F. M. Freitas, and D. J. Patel

Thursday—8:00 P.M.

Electron Magnetic Resonance

Applications of Electron Magnetic Resonance to Chemical and Biochemical Studies—E. D. Becker

The Role of EPR in Free Radical Chemistry—L. Piette

Electron Magnetic Resonance Studies of Free Radicals in Organic Crystals—T. Cole

The Application of Electrochemical Methods to the Study of Free Radicals by Electron Spin Resonance—A. H. Maki

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Pittsburgh Section

The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

Penn-Sheraton Hotel March 5-9, 1962

Symposia on Chemical Analysis of Metals, Gas Chromatography, Raman Spectroscopy, Spectroscopic Studies of Polymers, and Vacuum Spectroscopy are planned. In addition, original papers on all phases of analytical chemistry and spectroscopy are invited. The number of papers included in the program will be limited. All papers will be evaluated by the program committee before acceptance. The *absolute deadline* for receipt of abstracts is October 16, 1961.

Again this year the Exposition of Modern Laboratory Equipment will include more than 100 exhibitors. The Exposition will give an opportunity to see the latest in chemicals and equipment for analysis and permit personal discussion with the manufacturers.

Correspondence regarding papers should be submitted in duplicate to: Dr. C. F. Glick, Program Chairman, The Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Pa.

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News of Other Societies and Institutions

Editor—Raymond R. Sawyer

[Contributions to this column should be sent to the Editor, Mr. Raymond R. Sawyer, Columbia University, Hudson Laboratory, Dobbs Ferry, N. Y.]

General Electric Annual X-Ray Diffraction and Emission School

Milwaukee, Wisc. September 11-15, 1961

There will be a comprehensive review of fundamental x-ray physics and crystallography; theory of diffraction and emission; a review of instrumentation; and lecture-demonstration laboratory sessions on diffractometer, spectrometer, single crystal orienter, and film instruments.

Dr. David Harker, who has served as the main lecturer for nine years, will be joined by six invited guest speakers who will review their work in the x-ray field. Contact Mr. W. F. Loranger, X-Ray Department, General Electric Company, Milwaukee 1, Wisconsin.

Optical and X-Ray Quantometer School

Dearborn, Mich. October 2-6, 1961

This school will cover the fundamentals of emission spectroscopy and the instrumentation associated with it. Considerable time will be taken for the study of the equipment including training on methods of calibration, maintenance, and servicing procedures. The relationship between optical and x-ray applications will be covered and laboratory exercises dealing with all phases of the work will be included.

Contact Applied Research Laboratories, P. O. Box 1710, Glendale 5, California.

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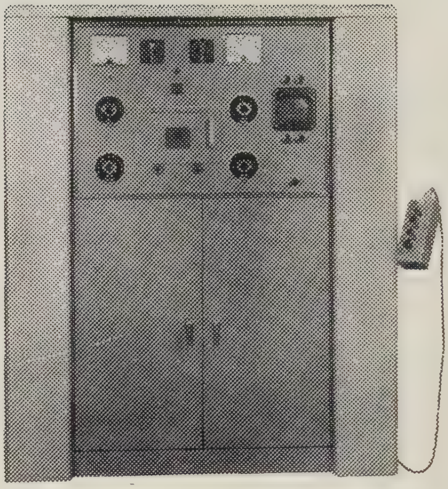

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Standard	*110-10	Upright	X	X	X	X	--	X	X	X
"	*110-91	"	X	X	X	X	--	X	X	X
"	110-92	"	X	--	--	--	X	--	--	X
"	110-93	"	X	--	--	--	--	--	--	X
"	110-94	"	X	X	X	--	--	--	--	--
"	110-97	"	--	--	--	--	--	--	--	X
"	110-81	"	X	X	X	X	--	X	X	X
"	110-82	"	X	--	--	--	--	--	--	X
"	110-83	"	X	X	X	--	--	--	--	--
Standard	110-910	Table Top	X	X	X	X	--	X	X	X
"	110-920	" "	X	--	--	--	X	--	--	X
"	110-810	" "	X	X	X	X	--	X	X	X
Compact	110-710	Sit Down	--	--	--	--	--	--	X	X
"	110-720	" "	--	--	--	--	--	--	--	X
"	110-730	" "	--	--	--	--	--	--	X	X
"	110-750	" "	--	--	--	--	--	--	X	X
Compact	*110-70	Upright	--	--	--	--	--	--	--	X
"	*110-71	"	--	--	--	--	--	--	X	X
"	*110-73	"	--	--	--	--	--	--	X	--
"	*110-76	"	--	--	--	--	--	--	--	X
"	*110-77	"	--	--	--	--	--	--	--	X
Spectrol	110-21	Portable	X	--	--	--	--	--	--	--
"	110-23	"	--	--	--	--	--	--	--	X

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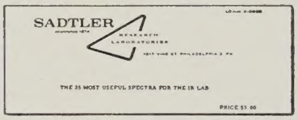
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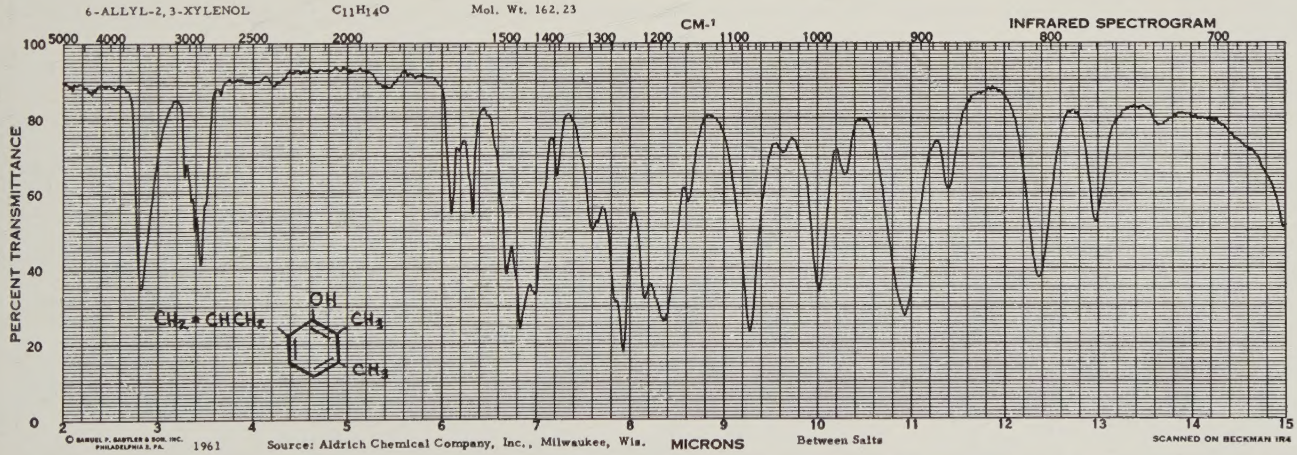

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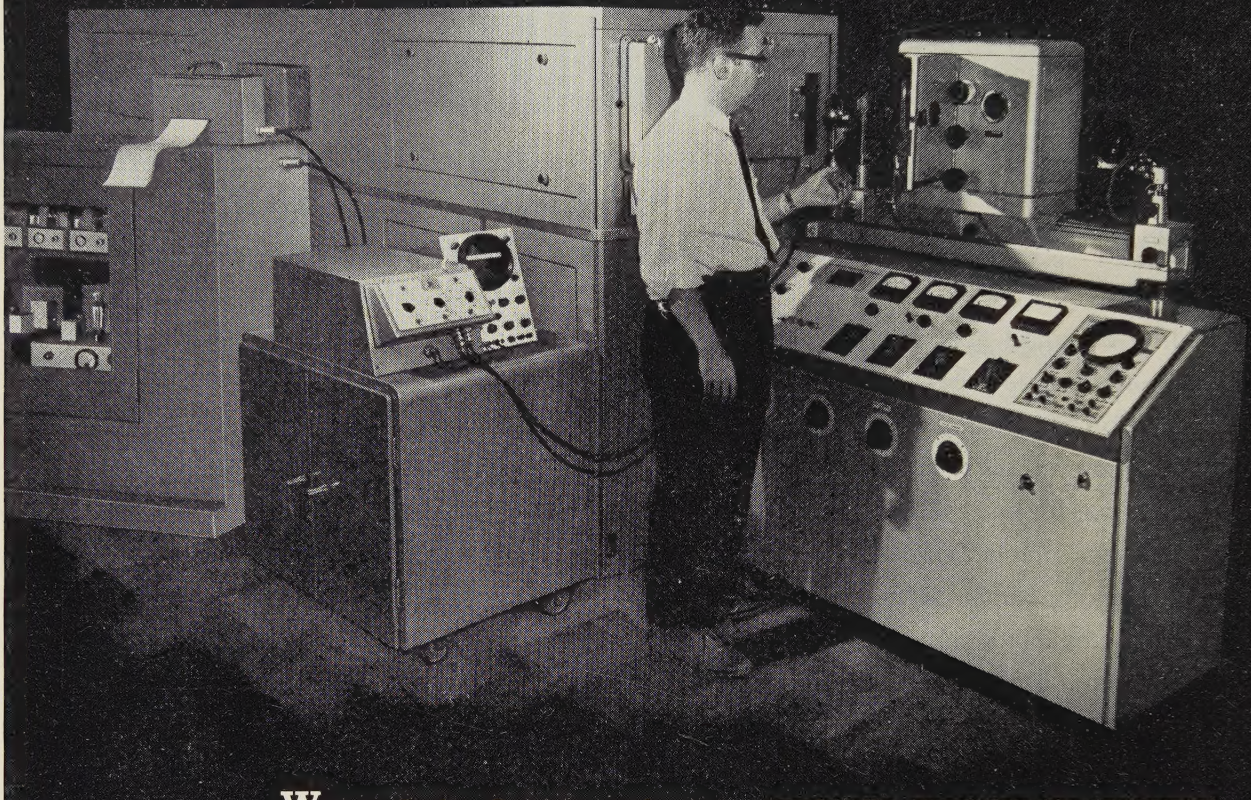

Wyman-Gordon Company produces a larger volume and wider variety of aircraft and missile forgings than any other metal fabricator in the world. Products include: fuselage frames (aluminum); landing wheels (magnesium); piston engine crankshafts (steel); turbine wheels (nickel-base alloy); missile re-entry shields (copper); and missile cones (titanium).

Such critical forgings demand the highest degree of quality control. Wyman-Gordon chose a Baird-Atomic Research Direct-Reading Spectrograph to do the job. With this instrument, one preset direct-reading head can be used for aluminum alloys, another for magnesium, a third for nickel, and so on. For non-routine or infrequent analyses, the unit can be used photographically, permitting one instrument to do the work of two. Changeover takes just 5 to 10 minutes.

More than 5,000 analyses are made on the Spectrograph each month . . . sometimes at the rate of one a minute. Its speed, flexibility and dependability play a key role in maintaining the quality and dependability of Wyman-Gordon forgings. This same quality control and time-saving convenience can be yours with a B/A Direct-Reading Spectrograph. Write for information.

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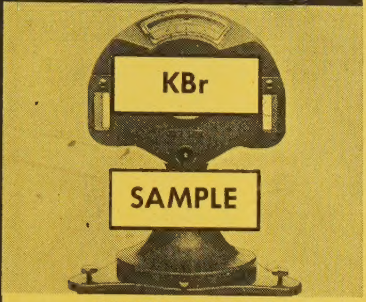

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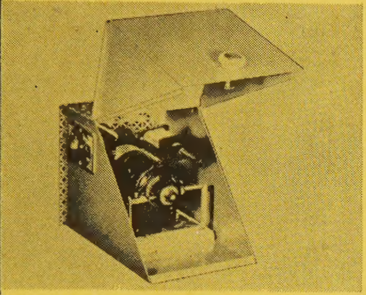

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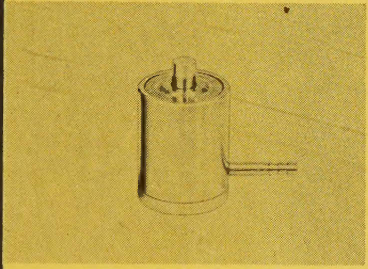

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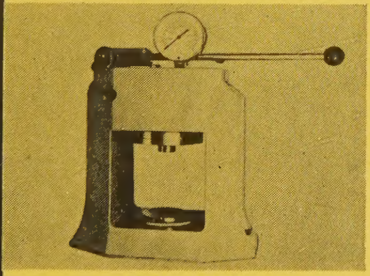

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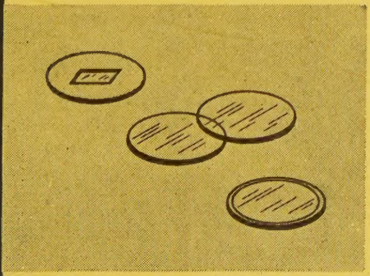

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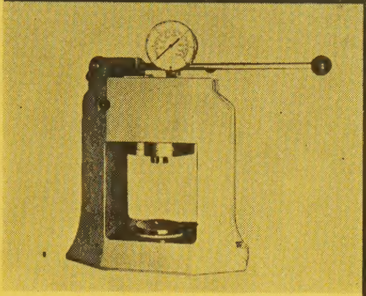
P.O. BOX 98 • SCOTCH PLAINS, N. J.

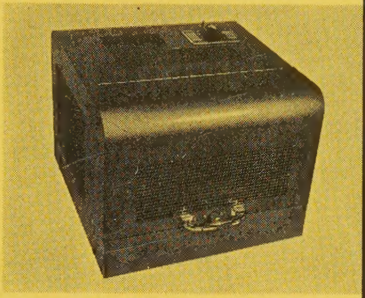
X-RAY

SPEXessories

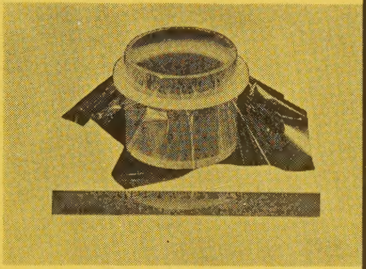
FOR G.E. X-RAY SPECTROMETERS



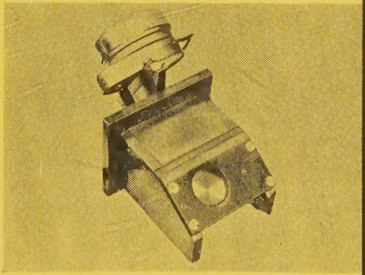
BRIQUETTING PRESS AND DIES



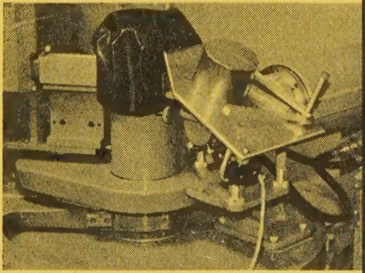
No. 8000 MIXER/MILL



EXPENDABLE LIQUID CELLS



TURNTABLE SAMPLE HOLDER



INVERTED BULK SAMPLE STAND

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COMPLETE CHEMICAL ANALYSIS IN SECONDS

Large expensive direct reading spectrometer installations have been in use by many large concerns. These investments have paid huge dividends by increasing the quality and quantity of many products.

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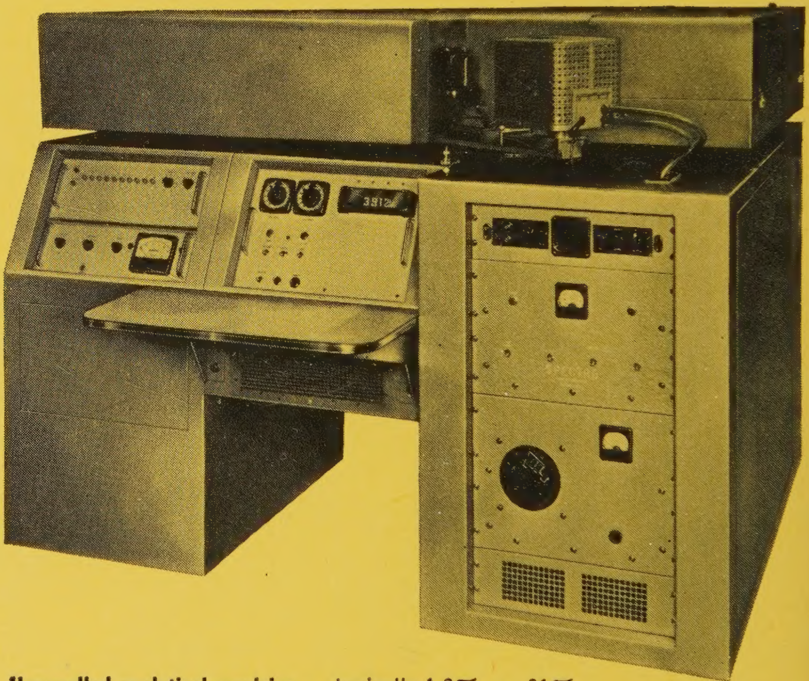

Unexcelled analytical precision — typically 1.0% ± .01%

Speed of analysis — complete 10 element analysis in 2-2½ minutes

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